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ROBERT M SALTER

SOIL SCIENCE

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Robert M. Salter

1892-1955

Robert M. Salter, chief of soils research for the U. S. Department of Agriculture and former head of the Soil Conservation Service, died September 13 at his home, 154 Colony Road, Silver Springs, Maryland. He was 63 years old.

Since November 1953, Dr. Salter had been chief of the Soil and Water Conservation Research Branch of the Department's Agricultural Research Service. Previously, he had served for two years as chief of the Soil Conservation Service.

Dr. Salter was one of the country's outstanding leaders in soil and plant research. His contributions in this field of endeavor are widely recognized. As a research administrator, he was noted for his sponsorship of the "whole-farm approach" to agricultural research, emphasizing the need for integrated application of new scientific developments for faster improvement of the many interdependent phases of farm operations.

A native of Huntington, Indiana, he grew up in northwestern Ohio and graduated from Ohio State University in 1913. Two years later he was awarded a master's degree, meanwhile serving as instructor in agricultural chemistry. From 1915 to 1921 he was at first chemist and later chairman of the soils department at the University of West Virginia.

Dr. Salter returned to Ohio State University as professor of soils in 1921. From 1925 to 1929 he was in charge of agronomic research for the Ohio Agricultural Experiment Station. He was promoted to chairman of the university's agronomy department in 1929 and to associate director of the experiment station in 1939.

In 1940, Dr. Salter became director of the North Carolina Agricultural Experiment Station. A year later he joined the U. S. Department of Agriculture in Washington, D. C., as head of the Division of Soils and Fertilizer Investigations in the former Bureau of Plant Industry. He became chief of the newly organized Bureau of Plant Industry, Soils, and Agricultural Engineering in 1942.

In 1944, Rutgers University, in recognition of his many contributions to agricultural science, awarded Dr. Salter the honorary degree of D.Sc. In 1952, he received the Department of Agriculture's Distinguished Service Award for his "leadership in agricultural research and the integration of research with other programs of agricultural production and conservation, contributing to the effective operation and management of American farms."

During his career in active research work, Dr. Salter made many important contributions to our knowledge of the chemical constitution of soils, the use of liming materials and fertilizers, and the general effects of the several types of farming systems on the level of productivity of the land. He was an independent

thinker and, in his early days, an excellent laboratory technician. He was outstandingly successful as an administrator.

Dr. Salter was a former president and fellow of the American Society of Agronomy, an officer and fellow of the American Society for the Advancement of Science, and a member of the National Research Council, Soil Science Society of America, Soil Conservation Society of America, Sigma Xi, and Phi Lambda Epsilon.

He is survived by his wife, Sara Godfrey Salter, and their four children, Mrs. Francis T. Phillips, Jr., of Omaha, Nebraska; Robert M. Salter, Jr., of Pacific Palisades, California; Richard G. Salter, of Cleveland, Ohio; and Mrs. E. Broadus Browne, of Athens, Georgia.

L. E. CHILDERS

WATER TABLES, EQUIPOTENTIALS, AND STREAMLINES IN DRAINED SOIL WITH ANISOTROPIC PERMEABILITY

D. H. EDWARDS

A.R.C. Unit of Soil Physics, Cambridge, England[1]

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It is commonly assumed that most soils in their natural state exhibit to some degree anisotropic properties with respect to hydraulic permeability. And there appears to be a prima facie justification for this view, since packings of an assemblage of particles may be envisaged whose pore-space configuration would be expected to confer a directional dependence on the permeability. Again the structure of a homogeneous soil may be broken up by fissures, caused by seasonal changes of moisture content and temperature, with resultant cycles of swelling and shrinkages. A differentiation of these phenomena would be expected between different directions, being most pronounced between the vertical and horizontal, which would thus give rise to differences in permeability between different directions. Accounts of measurements, however, which purport to give evidence for the existence of anisotropy in natural soils are few, because until recently there have been no field methods capable of resolving the measured apparent permeability into its axial components. Some progress, however, has been made in this direction. With their piezometer method Reeve and Kirkham (10) have successfully interpreted the results for certain soils as being indicative of anisotropy, and Boodt and Kirkham (1) have used this method to determine the ratio of horizontal to vertical permeabilities to air for a large extracted air-dried sample. Childs (6) has described a method which, when used in conjunction with Kirkham's piezometer method, enables an accurate estimate to be made of the axial permeabilities of a saturated triaxially anisotropic soil in the field. This latter method has been successfully employed in a preliminary survey of different soil types; one particular marsh peat was found to have a horizontal permeability of about 30 times that of the vertical. But until further evidence is obtained from field work, little more can be said concerning the frequency of incidence, nature, and degree of anisotropy.

Here we shall examine how the presence of anisotropy in soil affects flow in the ground-water zone in some typical two-dimensional steady-state drainage problems. Evidently the water table and flow net (pattern of streamlines and equipotentials) corresponding to an isotropic medium will be modified to an extent dependent upon the magnitude and orientation of the anisotropy. Only the following two cases were investigated: $K_x/K_y = 10$ and $K_y/K_x = 10$, where K_x and K_y are the permeabilities in the x and y directions, respectively, and K is defined by the equation

$$v = -K \operatorname{grad} \phi \tag{1}$$

[1] Present address: department of physics, University College, Aberystwyth, Wales. The author is greatly indebted to Dr. E. C. Childs, Director, A.R.C. Unit of Soil Physics, for his help and advice throughout the course of this work.

where v is the velocity of flow in cc./sec./unit cross section normal to the direction of flow, and ϕ is the potential in ergs per unit volume of fluid.

It can easily be demonstrated that a potential flow problem in an anisotropic space can be considered as a problem in an equivalent isotropic space in which the geometry of the boundaries has been suitably modified (2, 9, 11). Hence no special difficulties arise in the solution of problems in an anisotropic medium, for the methods of solution which are available for isotropic media are applicable. If (x, y) denote cartesian coordinates in the anisotropic space and (x_t, y_t) those of the isotropic transformed space, then the equations of the appropriate transformations are

$$x_t = \frac{x}{K_x^{\frac{1}{2}}} \quad \text{and} \quad y_t = \frac{y}{K_y^{\frac{1}{2}}} \tag{2}$$

If the potential difference between any pair of equipotentials in the (x_t, y_t) space remains the same as that between the corresponding pair in the (x, y) space, then the rate of flow in corresponding stream tubes in the two spaces is the same, provided that

$$K_t = (K_x K_y)^{\frac{1}{2}},$$

where K_t is the premeability in the isotropic transformed space. Hence, to determine the flow net for given boundaries in an anisotropic space, the boundaries must first be mapped according to equation (2) on the isotropic space (x_t, y_t) and the flow net determined there for the new boundaries. The required flow net is then obtained by transforming the flow net in the (x_t, y_t) plane back to the original (x, y) space.

Two-dimensional problems are conveniently studied by means of model experiments based on electrical analogy, in which appeal is made to the formal identity of D'arcy's law and Ohm's law, flow of fluid and hydraulic potential being hydrodynamic equivalents of electric current and electric potential, respectively. The manner in which the method can be applied to drainage problems has been described by Childs (3), who has used it to examine a wide range of such problems, including the case of nonsteady water tables after the commencement or cessation of rainfalls (4, 5, 6). Because of its flexibility and relative quickness, this method has been adopted in the present investigation in preference to numerical methods. Although numerical methods may claim freedom from the limitations imposed on the accuracy of the solutions by experimental equipment, since an accuracy of a few per cent is adequate, this advantage is inconsequential.

For the drainage problem to be amenable to a two-dimensional treatment, it is so formulated that uniform conditions obtain along the direction of the length of the drains. This implies that the length of the drain pipes is considerably greater than their separation and that the depth and permeability of the soil are uniform. The problem is further idealized by assuming the drains to be equidistant and of the same size with walls of infinite permeability; the effects of the capillary fringe are ignored and an equilibrium state is assumed to have been

achieved by a steady rainfall uniformly distributed over the water table. An assumption also implicit in the method is that the drains are running just full.

EXPERIMENTAL METHOD

The principles underlying the construction of an electric analogue of two-dimensional steady-state problems have been described by Childs (3), whose experimental procedure has been closely followed here. A commercially produced recording paper, "Teledeltos," one of whose surfaces is conducting, was employed in the construction of the analogue. This paper was found to fulfill satisfactorily the requirements of a good uniformity of resistance of reasonably high value to enable a sufficient accuracy to be attained in the measurement of potential; the maximum variation in its resistance is about 7 per cent, and the resistance, measured across a square, is approximately 1000 ohms. The "drain" electrode, through which the current is led out of the sheet, consisted of a brass plate about ⅛ inch thick, cut to scale to represent the drain. This electrode is held to the sheet by pressure applied through a spring-loaded screw arrangement mounted on fixed supports. Care was taken in machining the face of the electrode to ensure intimate contact with the paper at all points; this contact was further improved by applying a thin layer of diluted colloidal graphite to this face before placing the electrode in position.

The boundary conditions of an equilibrium water table require the corresponding locus of points in the analogue to satisfy the relation

$$V = Ah \qquad (3)$$

where V denotes the electric potential, h the height of a point above an arbitrary datum in the analogue of the original anisotropic space, and A an arbitrary constant; in addition, the current density must be uniform along its length. Such a locus is arrived at by a number of successive approximations which involve making adjustments to the lengths of the slits and the currents in the strips. In practice, two or three adjustments are usually found sufficient. After the analogue is constructed, the potential distribution over the whole sheet is investigated and the equipotential lines are plotted. Streamlines are then drawn in by eye (each streamline starting from the end of one of the slits) as a system of curves orthogonal to the equipotential curves.

EXPERIMENTAL RESULTS

In the first series of experiments the value of the horizontal permeability was chosen to be 10 times that of the vertical, or ($K_x/K_y = 10$); and in the second series the ratio of vertical to horizontal permeabilities was also taken to be 10, or ($K_y/K_x = 10$). In the solution of the former series the transformation described by equation (2) requires the boundaries to be distorted in such a manner that all dimensions in the x-direction are reduced by the ratio $(K_x)^{\frac{1}{2}}:1$, and dimensions in the y-direction reduced by the ratio $(K_y)^{\frac{1}{2}}:1$. This is evidently equivalent to multiplying all dimensions along the direction of the y-axis by the factor $(K_x/K_y)^{\frac{1}{2}} = 10^{\frac{1}{2}}$, while the dimensions along the x-axis are kept constant. Simi-

larly, for the case $(K_y/K_x) = 10$, the boundaries in the x-direction must be increased by the factor $10^{\frac{1}{2}}$ while those in the y-direction are retained at the the same value as in the original space. In particular, the circular perimeter of the drain is transformed into an ellipse, the ratio of whose major to minor axis is $10^{\frac{1}{2}}$ for $K_y/K_x = 10$ and vice versa for $K_x/K_y = 10$.

The drain separation is kept constant throughout at 10 m. and, as previously mentioned, S, the scale factor, is 1:50. Since the shape of the equipotentials and streamlines remains invariant with change of scale, the results may be interpreted to any desired scale.

The hydraulic counterpart of the boundary condition defined by equation (*3*) in the anisotropic space may be written as

$$\phi_{wt} = g\rho hS = \frac{g\rho VS}{A} \tag{4}$$

where ϕ is the hydraulic potential, g the acceleration due to gravity, and ρ the density of water. For any particular set of conditions the height of any one point on the water table above the datum may be chosen; for convenience, the point midway between the drain axes is selected. This choice automatically determines the value of the proportionality constant A for that experiment.

Streamlines and equipotentials are families of orthogonal curves in the transformed space which divide the field of flow into approximately rectangular areas. If an element of stream tube is defined as the volume swept out by one of these rectangular areas when displaced through unit distance normal to the plane of the paper, then such a volume element will be bounded by two stream surfaces of, for example, separation W, and two equipotential surfaces whose potential difference and separation are denoted by ϕ and L, respectively. Equality must obtain between the rates of flow in corresponding stream tubes in the anisotropic and transformed spaces. Hence if q_a denotes the rate of flow in a stream tube in the original (x, y) space, then the following relation holds for a volume element in the transformed space

$$\overline{(K_xK_y)^{\frac{1}{2}}} = \Delta\phi\cdot\left(\frac{W}{L}\right)$$

Since the area of the horizontal projection of the water table intersected by a stream tube in the original space is 50 sq. cm. it follows that $Q = q_a/50$, where Q denotes the rate of rainfall in cm./sec. Whence

$$\frac{Q}{(K_xK_y)^{\frac{1}{2}}} = \frac{\Delta\phi}{50}\cdot\left(\frac{W}{L}\right) \tag{5}$$

Some variation in the value of the ratio W/L is naturally found for different elements of stream tubes, because of experimental errors and slight departures from uniformity in the resistance of the sheet. Hence the mean value of a large number of elements is used for substitution in equation (*5*).

Hereafter in this paper, h_m will denote the height of the water table above the drain midway between the drain axes, h_d the height of the water table immedi-

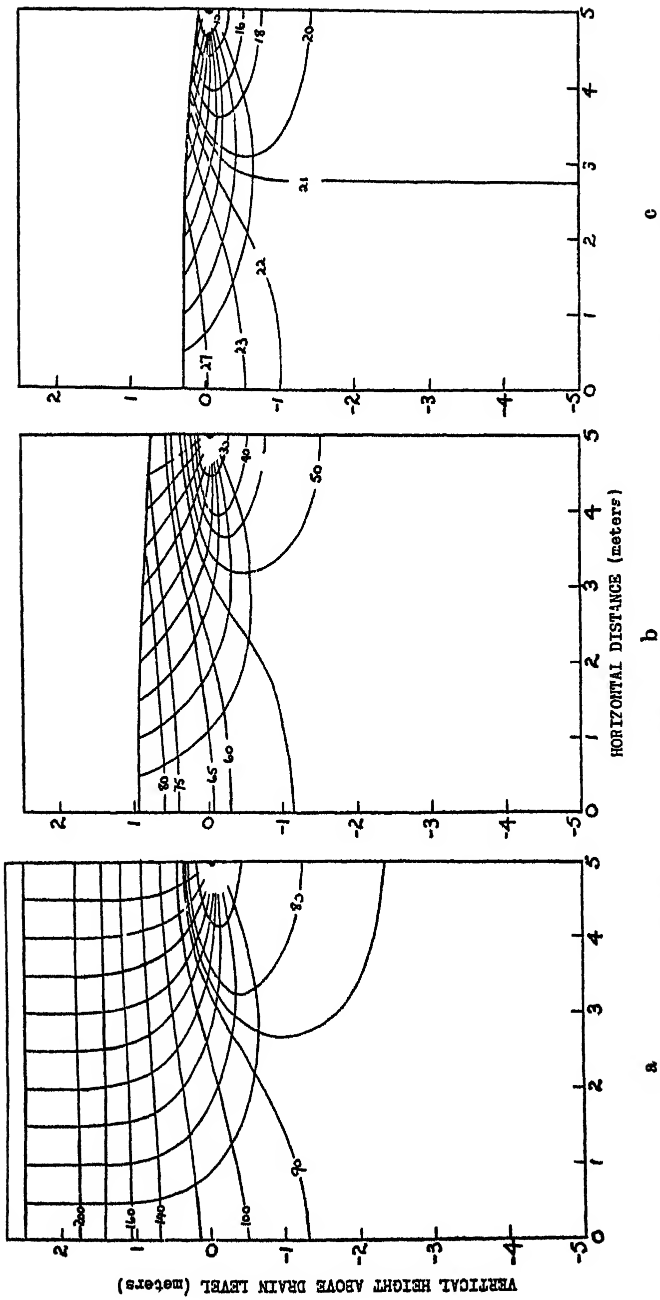


FIG. 1. FLOW DIAGRAMS FOR DRAIN DIAMETER OF 10 CM. WITH VARIED RAINFALL. $K_x/K_y = 10$.

ately above the drains, h_b the depth of the impermeable floor below the drain, and d the drain diameter. All dimensions quoted refer to actual dimensions of the drainage system.

Variation with rainfall

In the first series of experiments the smallest drain diameter of 10 cm. was used, the impermeable floor was maintained at a constant depth of 10 m. below the drain, and the amount of rainfall varied. For the case of $K_x/K_y = 10$ the flow diagrams are shown in figure 1, and the various quantities associated with these figures are given in table 1. The potential in all the diagrams is indicated in units of 1000 ergs per cc. Flow diagrams, with the same conditions, for a medium where $K_y/K_x = 10$ are shown in figure 5; the details of these diagrams are summarized in table 2.

TABLE 1

Dimensions of drainage systems in which horizontal permeability is 10 times that of vertical, or $K_x/K_y = 10$

Figure	d	h_m	h_d	h_b	$Q/(K_xK_y)^{\frac{1}{2}}$
	cm.	*m.*	*m.*	*m.*	*ergs/cc.*
1a	10	2.37	2.37	5	196.0
b	10	0.88	0.70	5	107.0
c	10	0.29	0.10	5	33.4
2a	30	1.22	1.11	5	176.2
b	60	1.03	0.83	5	184.0
3a	10	0.92	0.78	2	115.0
b	10	1.35	1.26	0	116.7
4a	10	3.16	3.16	0	182.8
b	30	1.90	1.82	0	177.0
c	60	1.38	1.25	0	175.3

TABLE 2

Dimensions of drainage systems in which vertical permeability is 10 times that of horizontal, or $K_y/K_x = 10$

Figure	d	h_m	h_d	h_b	$Q/(K_xK_y)^{\frac{1}{2}}$
	cm.	*m.*	*m.*	*m.*	*ergs/cc.*
5a	10	2.50	1.18	5	214.0
b	10	1.56	0.58	5	116.8
c	10	0.61	0.08	5	41.9
6a	30	2.13	0.31	5	224.0
b	60	1.73	0.30	5	187.8
7a	10	0.69	0.16	3	45.6
b	10	2.00	0.13	0	60.8
8a	30	2.05	0.08	0	81.6
b	10	3.55	1.00	0	160.0
c	10	2.55	0.38	0	96.0

Variation with drain diameters

In the next series of experiments the effect of varying the drain diameter was studied; the quantity of rainfall was kept constant and the impermeable bed was at the same depth below the drains as in the preceding series. Figure 2 shows diagrams for drain diameters of 30 cm. and 60 cm. when $K_x/K_y = 10$, the result for 10-cm. diameter drain having already been obtained in figure 1a.

The influence of drain size on the water table for $K_y/K_x = 10$ is shown in

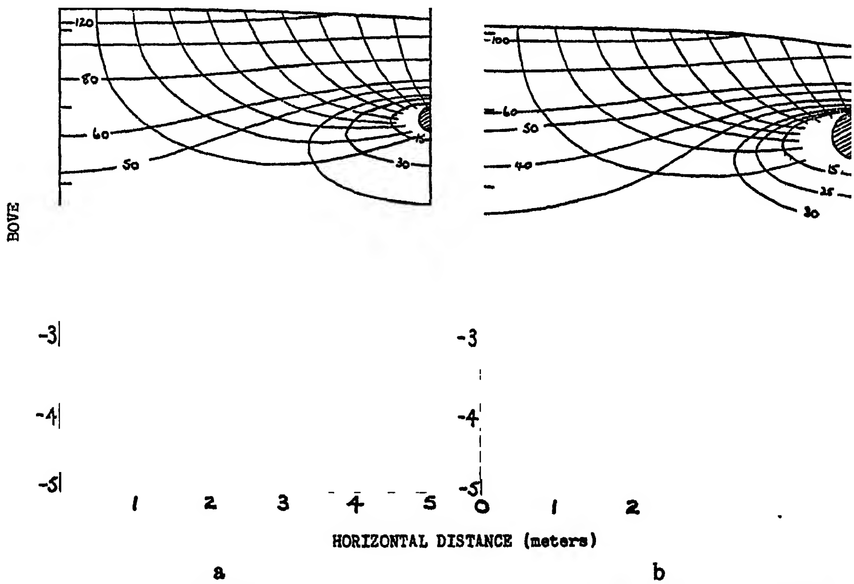


FIG. 2. FLOW DIAGRAMS FOR DRAIN DIAMETERS OF (a) 30 CM. AND (b) 60 CM. CONSTANT RAINFALL; $K_x/K_y = 10$.

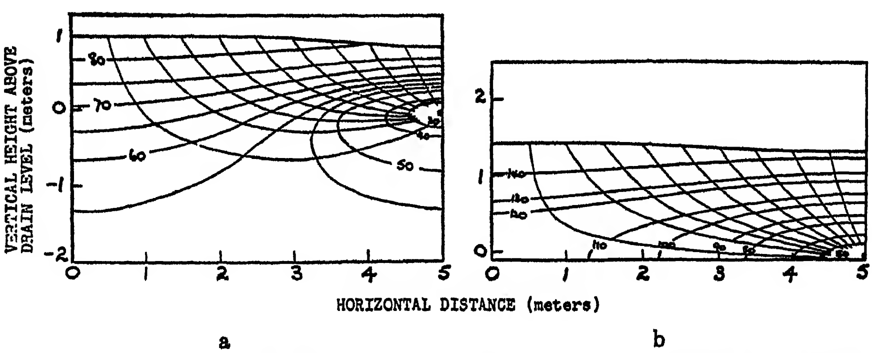


FIG. 3. FLOW DIAGRAMS FOR DRAIN DIAMETER OF 10 CM. (a) IMPERMEABLE BED AT DEPTH OF 2 M., (b) DRAIN RESTING ON IMPERMEABLE BED. $K_x/K_y = 10$.

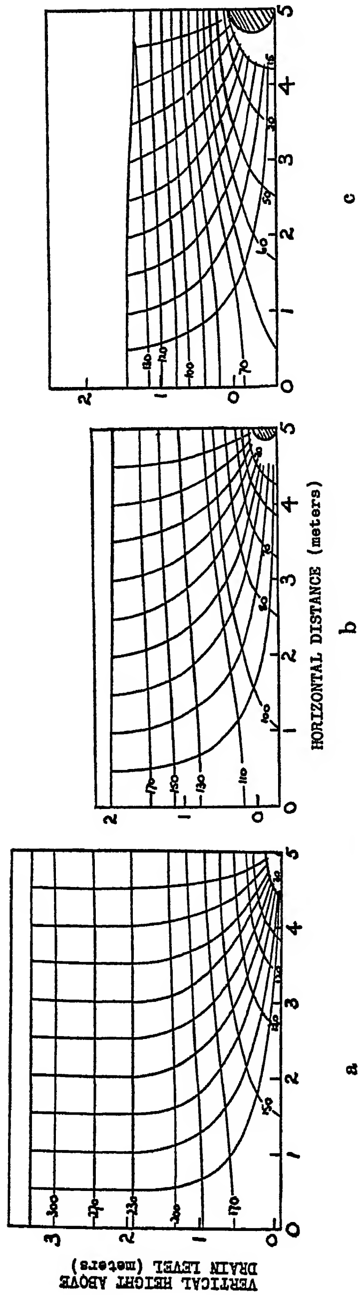
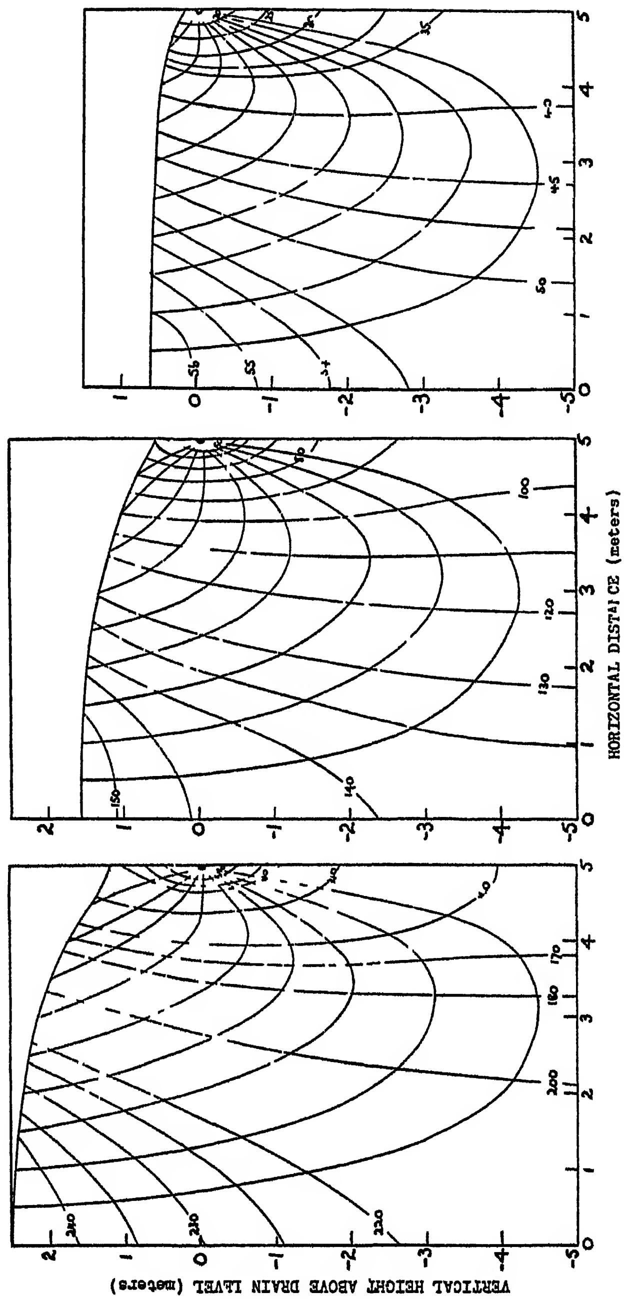


Fig. 4. Flow Diagrams for Drain Diameters of (a) 10 cm., (b) 30 cm., (c) 60 cm. Drains Resting on Impermeable Bed; Constant Rainfall; $K_x/K_y = 10$.



a b c

FIG 5 FLOW DIAGRAMS FOR DRAIN DIAMETER OF 10 CM. WITH VARIED RAINFALL $K_y/K_x = 10$

figure 6a and b; here again figure 5a of the preceding series must be used for comparison. Values for the diagrams in figures 2 and 6 are given in tables 1 and 2.

Variation with depth of impermeable floor below drain

The flow diagram in figure 3a is for a 10-cm. diameter drain with the depth of the impermeable bed reduced to 2 m. in a soil for which $K_x/K_y = 10$, and in

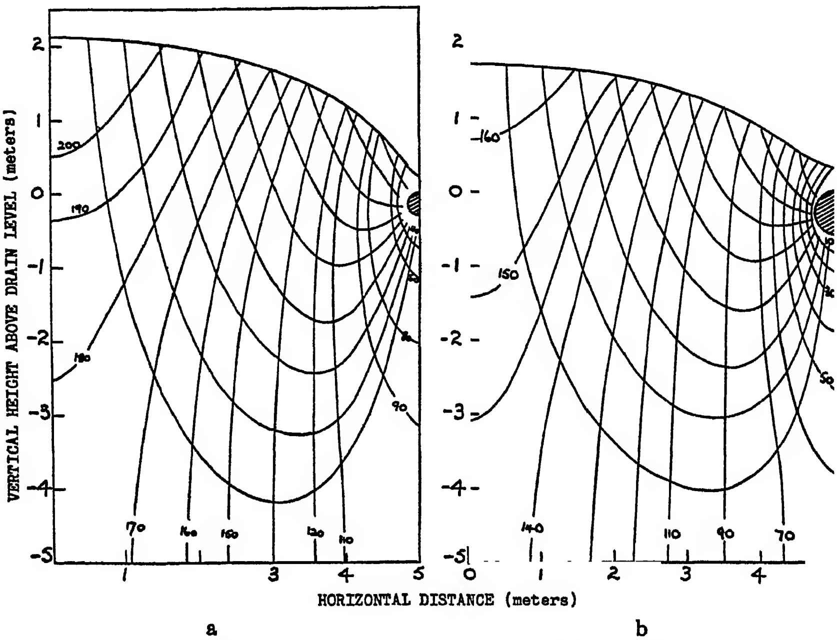


FIG. 6. FLOW DIAGRAMS FOR DRAIN DIAMETERS OF (a) 30 CM. AND (b) 60 CM. CONSTANT RAINFALL; $K_y/K_x = 10$.

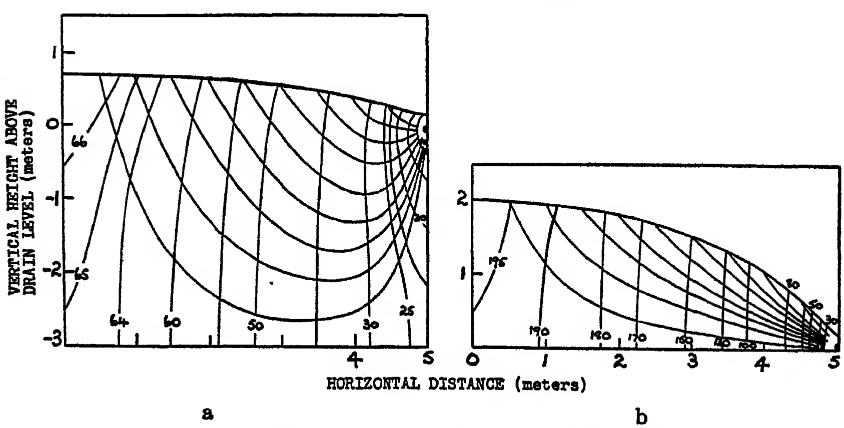


FIG. 7. FLOW DIAGRAMS FOR DRAIN DIAMETER OF 10 CM. (a) IMPERMEABLE BED AT DEPTH OF 3 M., (b) DRAIN RESTING ON IMPERMEABLE BED. $K_y/K_x = 10$.

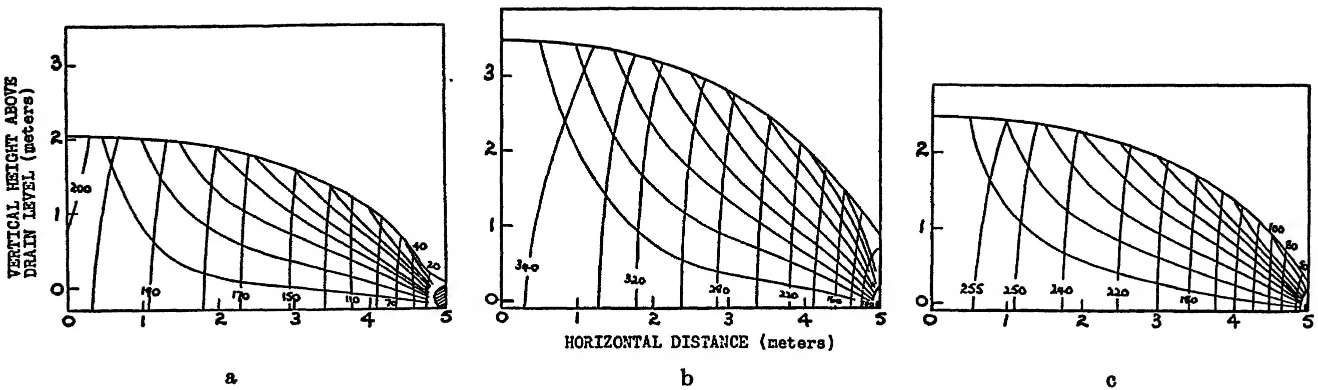


FIG. 8. FLOW DIAGRAMS FOR DRAIN DIAMETERS OF (a) 30 CM., (b) 10 CM., (c) 10 CM. DRAINS RESTING ON IMPERMEABLE BED; $K_y/K_x = 10$.

figure 3b the same drain is resting on the imperemable bed. The case in which the impermeable bed is at a depth of 5 m. has already been obtained in figure 1a. Flow diagrams for similar situations when $K_y/K_x = 10$ are given in figure 7a and b, in which the impermeable bed is at a depth of 3 m. and immediately below the drain, respectively. The diagram for the same drain diameter and rainfall, but with the impermeable bed 5 m. below the drain, is given in figure 5c. Tables 1 and 2 also give the relevant data for these diagrams.

Variation with drain diameter and rainfall for drains resting on an impermeable bed

In the final series of experiments several cases were investigated in which the drains were resting on the impermeable bed. Figures 4a, b and c show diagrams of three such cases for drain diameters of 10, 30, and 60 cm., when $K_y/K_x = 10$ and rainfall is maintained constant. Similar diagrams for $K_x/K_y = 10$ are given in figure 8a, b, and c. A description of these diagrams is given in tables 1 and 2.

DISCUSSION

The influence of anisotropic permeability in land drainage is more readily appreciated when the results reported are compared with those for isotropic soils. For this purpose, the results of Childs (3) and D'Oliveira e Sousa (7) have been employed. One method compares the results for an anisotropic medium with the results for two corresponding problems in isotropic media of which the permeability in one is equal to K_x and in the other to K_y. Suppose that the water tables, for particular values of d and h_b, in the two anisotropic cases considered here together with the water table in the corresponding isotropic case are matched

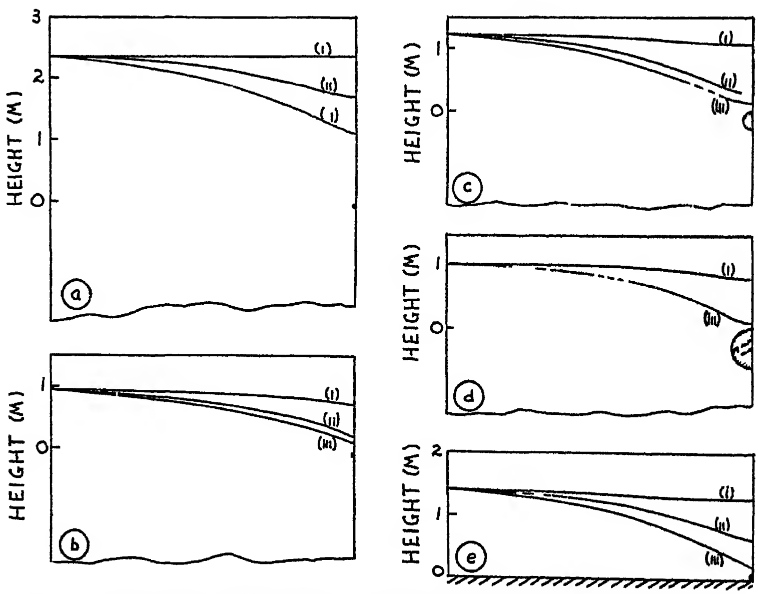


FIG. 9. COMPARISON OF WATER TABLES WITH THE SAME VALUE OF h_m

TABLE 3

Data relating to five cases depicted in figure 9

Fig.	d	h_b	h_m	h_d			Q			
				(i) $K_x/K_y = 10$	(ii) K_i	(iii) $K_y/K_x = 10$	(i) $K_x/K_y = 10$	(ii) $K_i = 10^{-7}$	(ii) $K_i = 10^{-8}$	(iii) $K_y/K_x = 10$
	cm.	*m.*	*m.*	*m.*	*m.*	*m.*	*cm./hr.*	*cm./hr.*	*cm./hr.*	*cm./hr.*
9a	10	5	2.37	2.37	1.73	1.11	0.022	0.091	0.009	0.023
b	10	5	0.90	0.70	0.20	0.11	0.012	0.031	0.003	0.007
c	30	5	1.23	1.10	0.33	0.12	0.024	0.054	0.005	0.017
d	60	5	1.00	0.82	—	0.10	0.021	—	—	0.013
e	10	0	1.41	1.27	1.13	0.03	0.013	0.027	0.003	0.004

at their midpoints, that is, each one is given the same value of h_m. From the results given by Childs and D'Oliveira it is possible to interpolate the appropriate values of Q/K_i for any given boundary configuration where the medium is isotropic. For example, when h_m is 2.5 m., the corresponding value of Q/K_i is found to be 266 ergs per cc. Accordingly, two rainfalls may be associated with the isotropic soil water table, 266 K_x cm./sec. and 266 K_y cm./sec., for comparison with the rainfalls in the anisotropic cases.

In figure 9 a series of water tables, which stand at the same height at the midpoint between the drain axes, are drawn for each of the three cases (i) $K_x/K_y = 10$, (ii) isotropic permeability, K_i, and (iii) $K_y/K_x = 10$. Here K_x and K_y have been allotted specific values typical of many medium soils; thus for $K_x/K_y = 10$, $K_x = 10^{-7}$ cgs., and $K_y = 10^{-8}$ cgs., and for $K_y/K_x = 10$, $K_y = 10^{-7}$ cgs. and $K_x = 10^{-8}$ cgs. The water tables in these two instances are compared with those in isotropic soils with permeabilities of 10^{-7} cgs. and 10^{-8} cgs. Values of the various parameters relating to the five cases shown in figure 9 are summarized in table 3.

It will be observed that when $K_x/K_y = 10$ the water tables do not deviate appreciably from a horizontal plane for values of h_m and d which are likely to occur in practice. In figure 9b and d, which are the lowest water tables considered, the difference between h_m and d is not large. On the other hand, large differences between h_m and h_d are obtained when $K_y/K_x = 10$; in general, they are more pronounced than those for isotropic soil. These differences in the gradients of the water tables depend on their heights above the drain and also on the position of the impermeable bed relative to the drain. It is also of interest to consider the relative magnitudes of the rainfall rates associated with the steady-state water tables of figure 9. For example, in figure 9a, where h_m is 2.37 m., the rainfall for case (i) is approximately the same as that in case (iii), and in figure 9b, where h_m is 0.90 m., the ratio of rainfalls is 1.7, that is, the discrepancy between the two cases increases as the height of the water table decreases. Furthermore, in figure 9a, the ratio of rainfall obtaining in case (i) to that in case (ii), with $K_i = 10^{-7}$ cgs., is 0.24 when h_m is 2.37 m., and in figure 9b it is 0.39 when h_m is 0.90 m. These data indicate that for low water-table heights the correspond-

ing value of rainfall is more dependent on the horizontal than the vertical permeability. As the water-table height increases, an increasing proportion of the length of the flow paths will be vertical, and the influence of the vertical permeability on the flow will consequently increase. When the drains approach an impermeable bed, a greater part of the flow occurs horizontally, and consequently the ratio of the rainfalls in case (i) to case (iii) increases; thus in figure 9c, where the drains are resting on the impermeable bed, this ratio is 3.25. These conclusions could, of course, be inferred qualitatively from an inspection of the flow nets of the various solutions.

The results of tables 1 and 2 may be expressed by presenting graphically the relationship between Q and h_m as in figure 10 for a value of $d = 10$ cm. where K_x and K_y are given the same values as in figure 9; the two isotropic cases are included for comparison. For the range of rainfall rates considered, h_m varies approximately linearly with Q in the isotropic cases and for $K_y/K_x = 10$. For $K_x/K_y = 10$, h_m is not linearly dependent on Q; the slope of the curve decreases as h_m increases until at a value of h_m of roughly 2.5 m. it coincides with the curve for $K_y/K_x = 10$. This fact is in accordance with the observation already made, that the greater the value of h_m the more the flow is governed by the vertical permeability.

The variation of h_m with drain diameter for each of the cases $K_x/K_y = 10$, $K_y/K_x = 10$, and isotropic is shown in figure 11. By choosing appropriate values for $Q/(K_xK_y)^{\frac{1}{2}}$ and Q/K_i, the corresponding values of h_m in each case are made to coincide at 2.5 m. for $d = 10$ cm. It will be noted that the drain diameter exercises a greater control over h_m when $K_x/K_y = 10$ than in the isotropic medium or when $K_y/K_x = 10$, the variations with diameter in the latter cases being of similar magnitude.

When the depth of a horizontal impermeable bed below the drain level is decreased, the field of flow is restricted and the flow net thereby modified; this results in the elevation of the water table for a given rainfall. The extent of the modification of the flow net will depend on its characteristics, being large where

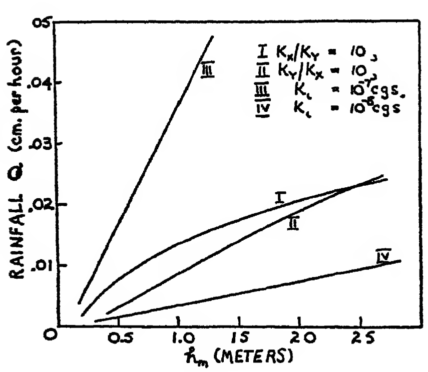


FIG. 10

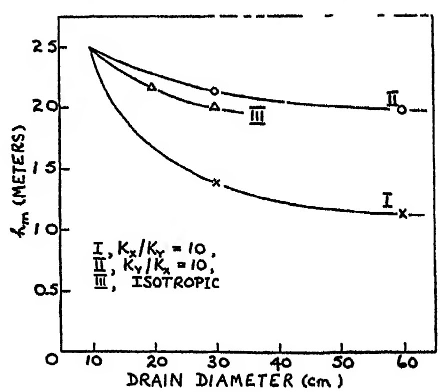


FIG. 11

FIG. 10. VARIATION OF h_m WITH RAINFALL
FIG. 11. VARIATION OF h_m WITH DRAIN DIAMETER

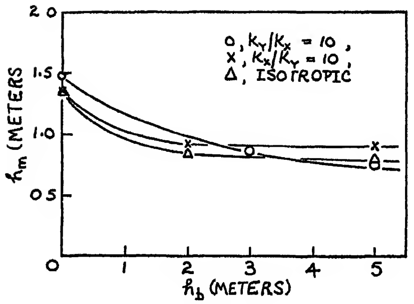


FIG. 12

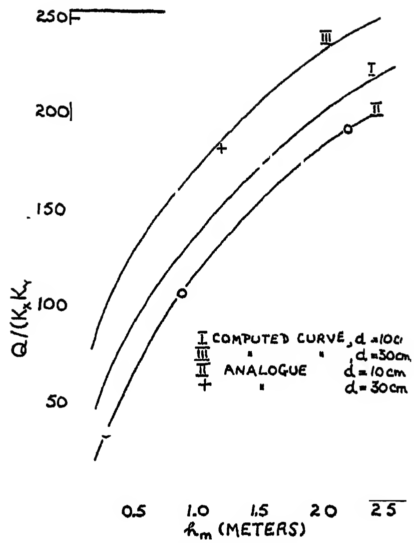


FIG. 13

FIG. 12. VARIATION OF h_m WITH DEPTH OF IMPERMEABLE BED BELOW DRAIN FOR $d = 10$ CM.

FIG. 13. COMPARISON OF ANALOGUE RESULTS WITH THOSE GIVEN BY ENGELUND'S THEORY FOR $K_x/K_y = 10$

the flow extends to some depth below the drain and small when the flow is confined to a depth of soil only a little below drain level. The former property belongs to the flow net when $K_y/K_x = 10$, and the latter when $K_x/K_y = 10$. The curves in figure 12 show that the effect of the proximity to the drain of an impermeable layer is least when $K_x/K_y = 10$, becoming significant only at a depth of approximately 1.5 m. A similar, although slightly greater, effect is obtained in the isotropic soil, where the change in h_m begins at a depth of 2 m. When $K_y/K_x = 10$, however, the influence of the impermeable bed on h_m is noticeable at roughly twice this depth, namely 4 m.

By applying established methods in potential theory, Engelund (8) has derived solutions for the steady-state drainage problem in an anisotropic soil where K_x is greater than K_y, and on the assumption that the water table lies in a horizontal plane. Since the water tables in a soil for which $K_x/K_y = 10$ are virtually horizontal, even at low values of h_m, there appears to be some justification for applying the plane water table formulas in this case. Curve I of figure 13 shows values of $Q/(K_xK_y)^{\frac{1}{2}}$ calculated from Engelund's theory for different heights of the plane water table, and curve II is derived from the results of the present analogue experiments; the agreement is fairly close. Curve III in the same diagram is the calculated curve for $d = 30$ cm.; here, though we have only one analogue result for comparison, the agreement is again satisfactory.

SUMMARY

Two-dimensional steady-state drainage problems are investigated by the method of electric analogues for a soil whose permeability is anisotropic. Solu-

tions for two values of anisotropy are presented, $K_x/K_y = 10$ and $K_y/K_x = 10$, where K_x and K_y denote, respectively, the horizontal and vertical components of permeability. In each case it is shown: (*a*) how the height of the water table varies with the rate of rainfall for a particular drain diameter; (*b*) the manner in which the drain diameter is related to the water table height for a given rainfall; and (*c*) how an impermeable bed below the drains influences the flow. The results are discussed by comparing them with published results for isotropic soils. An analytical solution, which is valid for the hypothetical situation of a plane water table and when K_x is greater than K_y, is shown to be in reasonable agreement with the present analogue results.

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DESALINIZATION OF SALINE SOILS AS A COLUMN PROCESS

W. H. van der MOLEN

Research Department Noordoostpolder Authority, Kampen, Holland

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In 1944 large areas in the southwestern part of the Netherlands were inundated with sea water for military purposes. After these soils were drained an extensive study was made of their desalinization under the influence of the moist Dutch climate (mean annual precipitation about 700 mm.).

The numerous observations on soil salinity made during these years have been analyzed by Verhoeven (7, 8). From these observations conclusions could be drawn concerning evapo-transpiration, capillary rise, and downward movement of water in these soils.

In addition to these observations, many analyses were made on the exchangeable cations in the flooded soils and their changes after drainage. In working out these data it became clear that the behavior of these ions could be understood only if the soil was regarded as analogous to an ion-exchange column. As the theory of column performance has been well developed (2, 3, 4, 9), its usefulness for describing the conditions prevailing in soils may be tested by comparing the observed changes with those required by theory.

In this article application of the theory of column operation to desalinization of soils under the influence of passage of water vertically downward is treated. The results of the application of the theory to ion-exchange processes will be published elsewhere.

THEORIES OF COLUMN OPERATION

In theory, column performance depends largely on the shape of the adsorption isotherms (2). For compounds that are not adsorbed by the soil particles—like the Cl ion—these isotherms may be considered as linear, as a division of the solute will be set up between the soil moisture retained by the soil and the moisture percolating through the profile. This process, therefore, might be treated according to the theory of Martin and Synge (4), developed for partition chromatography. In this theory the column is considered as being composed of a number of plates of finite and equal thickness, at each of which complete equilibrium is set up. But, the discontinuous probability distribution following from this theory is rather cumbersome to handle in practice.

In the theories of Wilson (9) and De Vault (2), recently applied to soil columns by Ribble and Davis (6), an infinitesimal thickness of the theoretical plates is assumed. For linear adsorption isotherms, this theory predicts that in the course of the leaching process the shape of the boundary remains unchanged.

This, however, is not the case in practice, even in laboratory columns operating under ideal circumstances. Obviously disturbing factors are operative in actual columns. According to Glueckauf (3), these disturbances may be caused

by the following factors: finite grain size, diffusion in the liquid between the grains, and nonequilibrium conditions.

For columns in which only the first two of these factors are operative, Glueckauf (3) derived a differential equation which could be solved for a linear adsorption isotherm. As in soils leached under natural conditions the streaming velocity is extremely small (under Dutch conditions maximally of the order of 2 ml. per sq. cm. per 24 hours and of the order of 20–30 ml. per sq. cm. annually), it is not likely that nonequilibrium conditions will be important. Only in heavy soils, with a clay content above 20 per cent, are large cracks likely to be present, which allow a rapid downward movement of water. In such soils, nonequilibrium between the penetrating water and the soil moisture in the layers passed by may be of practical importance. In other cases, however, diffusion will be one of the principal disturbing factors, though irregularities in soil permeability causing irregular flow, will also play their part (8). Nevertheless, it may be expected that the Glueckauf theory will be applicable to the conditions in soils. Only by testing the theory in observed cases may the role of the disturbing factors be traced.

THE GLUECKAUF THEORY

The following notation will be used:

v:	volume of rain water passing through the soil (ml. per sq. cm.). The Cl^- content of this water may be taken as zero.
$x = \rho d$:	weight of soil below soil surface per unit area (g. of dry matter per sq. cm.).
d:	distance from the soil surface (cm.).
ρ:	density of the soil (g. of dry matter per cc.). In Dutch sea-clay soils the value $\rho = 1.4$ may be used.
c:	concentration of the Cl ion in the soil moisture (mg. per ml.).
c_0:	initial concentration of the Cl ion in the soil moisture (mg. per ml.). This initial concentration is supposed to be uniform throughout the profile.
$f^*(c)$:	quantity of ions adsorbed by the soil in equilibrium with a solution of concentration c (mg. per g. of dry matter). For the Cl ion, which is not adsorbed by the soil,[1] $f^*(c)$ is obviously equal to zero.
$f(c) = f^*(c) + \alpha c$:	total quantity of ions present in the soil (mg. per g. of dry matter).
α:	pore space filled with liquid (ml. per g. of dry matter).
$2k' = 2\rho k$:	weight of theoretical plate per unit area (g. of dry matter per sq. cm.).
$2k$:	height of theoretical plate (cm.).
$N = x/2k' = d/2k$:	number of theoretical plates above depth x or d respectively.
$A = 100\alpha$:	moisture content of the soil (ml. per 100 g. of dry matter).

[1] Actually the Cl ion shows a slight negative adsorption, which is the counterpart of the positive adsorption of cations. This negative adsorption, however, does not greatly affect its behavior, as in Dutch saline soils usually more than 90 per cent of the soil moisture may be regarded as freely accessible to Cl ions (10). In all calculations treated in this article, therefore this negative adsorption has been disregarded.

B: salt content of the soil (Cl^-, expressed as g. of NaCl per 100 g. of dry matter).

B_0: initial salt content of the soil (Cl^-, expressed as g. of NaCl per 100 g. dry matter).

$C = (1000\ B)/A$: salt concentration in the soil moisture (Cl^-, expressed as g. of NaCl per l. of soil moisture).

From the foregoing it follows that

$$f(c) = \alpha c = \frac{Ac}{100} \tag{1}$$

Further when

$$\bar{v} = \alpha x = \alpha\rho\, d = 0.014\, Ad \tag{2}$$

and

$$\bar{v} \qquad 0.014\, Ad \tag{3}$$

the solution of the differential equation

$$\left(\frac{\partial f}{\partial v}\right)_x + \left(\frac{\partial c}{\partial x}\right)_v - k\left(\frac{\partial^2 c}{\partial x^2}\right)_v = 0 \tag{4}$$

for the case of desalinization of a homogeneously saline profile may be represented by

$$c = \frac{c_0}{2}\left[\operatorname{erfc}\frac{p-1}{\sqrt{2p}}\sqrt{N} - e^{2N}\operatorname{erfc}\frac{p+1}{\sqrt{2p}}\sqrt{N}\right] \tag{5}$$

in which erfc denotes the error function complement[2]:

$$\operatorname{erfc} n = 1 - \frac{2}{\sqrt{\pi}}\int_0^n e^{-u^2}\,du \tag{6}$$

At large values of N (without too large errors for $N > 4$) the second term in equation (*5*) may be disregarded[3], so that:

$$c = \frac{c_0}{2}\operatorname{erfc}\frac{p-1}{\sqrt{2p}}\sqrt{N} \tag{7}$$

A nomogram for this function is represented in figure 1. Assuming the moisture content of the soil during the leaching process to be constant, this equation may also be written as:

$$B = \frac{B_0}{2}\operatorname{erfc}\frac{p-1}{\sqrt{2p}}\sqrt{N} \tag{8}$$

[2] The function $E_2(n) = \frac{2}{\sqrt{\pi}}\int_0^n e^{-u^2}\,du$ has been extensively tabulated, for example, by Jahnke and Emde (5). Moreover a table for erfc (n) has been given by Carslaw and Jaeger (1).

[3] The second term in equation (*5*) reaches its maximum at $p = 1$; in that case it becomes $e^{2N}\operatorname{erfc}\sqrt{2N}$, which, for not too small values of N approaches $\frac{1}{\sqrt{2\pi N}}$.

It follows from equation (*8*) that:

$$B = \frac{B_0}{2} \text{ at } p = 1 \text{ or at } v = \bar{v} = 0.014\, Ad \text{ (ml. per sq. cm.)} \tag{9}$$

From equation (*9*) the volume of water needed to reduce the salt content at a certain depth to half its initial value may be predicted theoretically.

The value of N may be derived either from curves of B against v at constant depth or from curves of B against d at constant v. The slope of these curves at the point where $B = \frac{B_0}{2}$ may be measured; from this slope the value of N may be calculated according to the following equations:

$$N = 2\pi \left[\frac{v}{B_0} \cdot \frac{\partial B}{\partial v}\right]^2_{B=B_0/2} \tag{10}$$

$$N = 2\pi \left[\frac{d}{B_0} \cdot \frac{\partial B}{\partial d}\right]^2_{B=B_0/2} \tag{11}$$

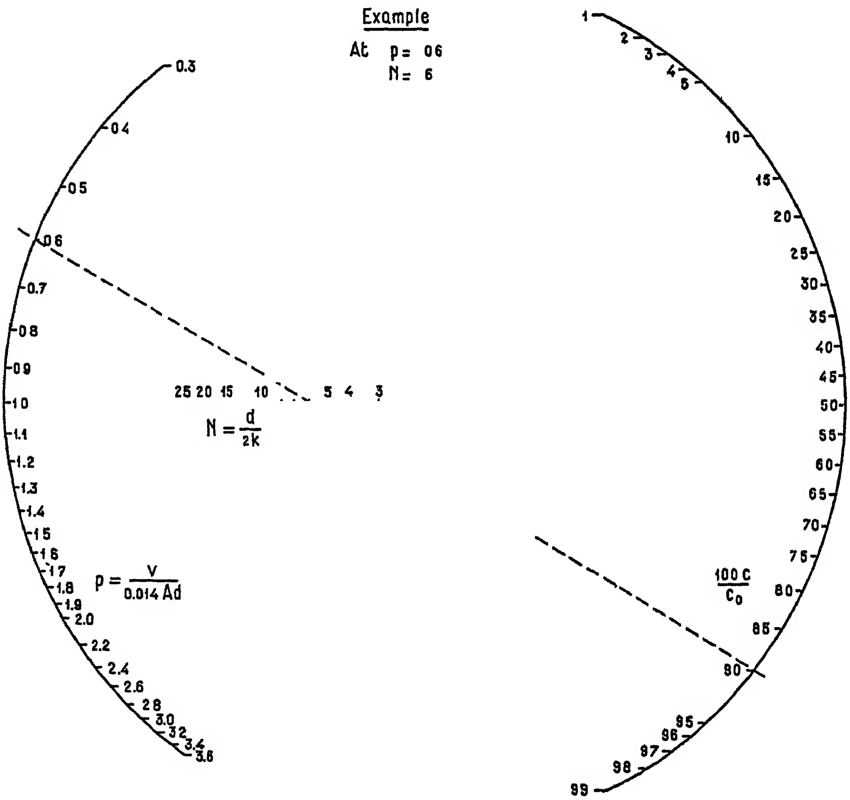

FIG. 1. NOMOGRAM OF THE FUNCTION $c \quad c_0/2 \text{ erfc } \frac{p-1}{\sqrt{2p}} \sqrt{N}$

(EQUATION 7)

AVAILABLE OBSERVATIONS

The salinity data used for testing the theory were obtained by periodical sampling of fixed spots to a depth of 80 cm. In the samples, moisture content (A) and salt content (B) were determined, after which the salt concentration in the soil moisture (C) could be calculated. From these data the amounts of water that had passed through the soil between two samplings could be derived by dividing the salt losses from the upper part of the profile (usually the 0–60-cm. layer) by the average salt concentration at the bottom of the profile (usually the 60–80-cm. layer). More details concerning this method, its errors and its imitations, have been given by Verhoeven (7, 8).

As appears from these observations, desalinization in Holland occurs only during the winter months (October–March); during this period the moisture content of the soil (A) may be regarded as constant. Hence, equation (*8*) can be applied, at least for the deeper layers where N is fairly large.

Of the many sampling spots investigated after the 1944–45 inundations, however, only a few may be considered to be homogeneous in salt content at the beginning of the observations. It stands to reason that these homogeneously saline profiles are especially suited for testing the theory of column operation.

APPLICATION OF THE THEORY

By the aforementioned observations, empirical relations are established between B and v at constant depth and between B and d at constant and known values of v. These observations may therefore be used for checking the theory in the following ways:

1. By comparing the calculated values of $\bar{v}$ $\left(\text{at which } B = \frac{B_0}{2}\right)$, as obtained from equation (*9*), with those observed. As the simplified equation (*8*) is not valid for low values of N, the top layers should be excluded from this comparison.
2. By comparing the values of the theoretical plate thickness ($2k$) obtained from equation (*10*) with those obtained from equation (*11*).
3. By comparing the observed general trends of the desalinization process with those required by theory.

As an example, the results obtained for the sampling spot OB 3 will be treated in more detail. The observed salinity-water passage curves for this spot are represented in figure 2A, together with the salinity-depth curves at two different dates.

For the application of the theory, the profile has been considered as being homogeneously saline at the beginning of the observations, with a salinity of $B_0 = 0.50$. During the desalinization period, the moisture content appeared to be rather constant, with an average of $A = 23.8$. For each layer sampled, the volume $\bar{v}$ at which B has been reduced to 0.25 may be either read directly from figure 2A or calculated according to equation (*9*). In the same way the volume v passed at the sampling dates December 17, 1947 and January 21, 1948 may

be calculated either from the salinity data themselves or, theoretically, by means of equation (9), from the depth at which B has become equal to 0.25.

As appears from table 1, excellent agreement exists between the observed values of v and those predicted by the column theory.

The value of the theoretical plate thickness has been calculated in four different ways, namely:

1. From the desalinization of the 40–60-cm. layer. By application of equation (10) N was found to be 16, corresponding with a theoretical plate thickness of 3.1 cm. or 4.4 g. per sq. cm.

2. From the desalinization of the 60–80-cm. layer. By application of equation (10) N was found to be 57, corresponding with a theoretical plate thickness of 1.2 cm. or 1.7 g. per sq. cm.

3. From the salinity-depth curve of December 17, 1947. By application of equation (11) N was found to be 10 at $d = 42$ cm. These data correspond with a theoretical plate thickness of 4.2 cm. or 5.9 g. per sq. cm.

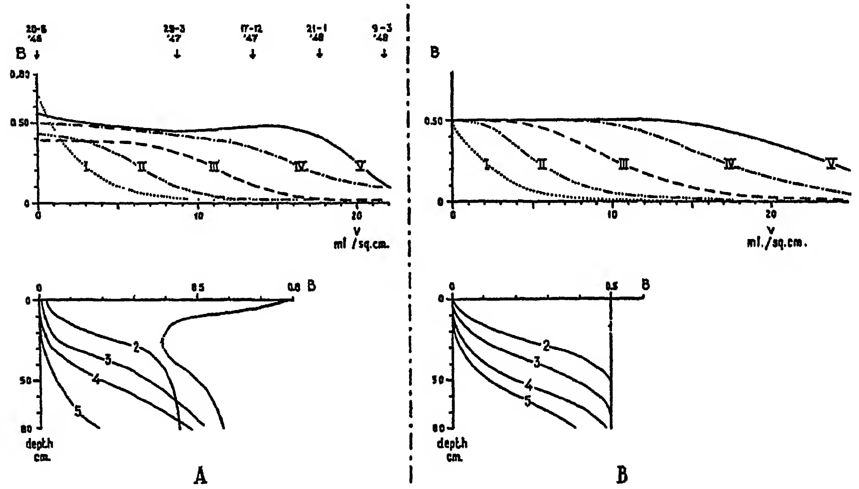

FIG. 2. DESALINIZATION ON SAMPLING SPOT OB 3

Sampling dates: 1, June 20, 1946; 2, March 29, 1947; 3, December 12, 1947; 4, January 21, 1948; 5, March 9, 1948. Layers sampled: I, 0–10 cm.; II, 10–20 cm.; III, 20–40 cm.; IV, 40–60 cm.; V, 60–80 cm.

A: observed; B: calculated from equation (7) with $A = 23.8$; $B_0 = 0.50$; $2k = 5$ cm.

TABLE 1

Observed and calculated values for v at sampling spot OB 3, light soil

Layer	$\bar{v}$ (ml. per sq. cm.)		Date of Sampling	v (ml. per sq. cm.)	
	Observed	Calculated from eq. (9)		Calculated from salinity data	Calculated from eq. (9)
cm.					
20–40	10.5	10.0	Dec. 17, 1947	13.4	14.0
40–60	16.0	16.7	Jan. 21, 1948	17.6	18.7
60–80	20.0	23.4			

TABLE 2

Observed and calculated values for v at sampling spot OB 23, heavy soil

Layer	$\bar{v}$ (ml. per sq. cm.)		Date of Sampling	v (ml. per sq. cm.)	
	Observed	Calculated from eq. (*9*)		Calculated from salinity data	Calculated from eq. (*9*)
cm.					
10–20	±10.0	5.5	Jan. 21, 1948	25.1	23.5
20–40	15.0	10.7			
40–60	20.0	18.4			
60–80	25.5	25.7			

4. From the salinity-depth curve of January 21, 1948. By application of equation (*11*) N was found to be 11 at $d = 56$ cm. These data correspond with a theoretical plate thickness of 5.1 cm. or 7.1 g. per sq. cm.

With the exception of No. 2, the values for $2k$ are reasonably in accord with one another; obviously, the salinity curve for the 60–80-cm. layer has been influenced by experimental errors. As the values for $\partial B/\partial v$ and $\partial B/\partial d$ must be squared, the value of N is very sensitive to errors of this kind.

The general shape of the curves, predicted by theory, is in fair agreement with the empirically established course of the desalinization process, as may be seen by comparing the observed curves from figure 2A with the theoretical curves represented in figure 2B. The latter have been calculated for $A = 23.8$, $B_0 = 0.50$, $2k = 5$ cm., with the help of equation (*8*).

From the other cases tested, it appeared that in light soils, with a clay content below 20 per cent, usually a fair agreement exists between the values of $\bar{v}$ calculated from equation (*9*) and those observed; their mutual difference seldom exceeds 20 per cent of the theoretical value. In heavier soils, however, desalinization of the upper layers appeared to proceed much more slowly than required by the theory (table 2).

This divergence must be attributed to the presence of cracks in these soils; obviously part of the rainfall, passing rapidly through these cracks, does not take part in the desalinization process.

For all cases observed, the theoretical plate thickness $2k$ proved to be approximately 5 cm., with most observations ranging between 4 and 7 cm. Moreover, the general trends of the process were in accordance with those predicted theoretically.

It may therefore be said that, at least for light soils, the theory gives a fair description of the phenomena observed in the desalinization of homogeneously saline profiles.

DESALINIZATION OF HETEROGENEOUSLY SALINE SOIL PROFILES

Where the initial salt content of the soil varies with depth, the principle of superposition may be used. In this case the soil is considered as the sum of a series of homogeneously saline profiles beginning at different depths. The desalinization of each of these imaginary profiles may be calculated according to the theory of column operation, after which the results may be added.

As an example, leaching of the salt from the sampling spot SJ 1 will be treated. The observed desalinization of this profile is reproduced in figure 3A.

For the calculation of the theoretical desalinization the observed initial distribution of the salt over the profile has been taken as a base. This initial situation has been analyzed by splitting up the profile into homogeneously saline profiles 0–80, 10–80, 20–80, and 40–80 cm. with salt contents B_0 of 0.50, −0.33 −0.03, and +0.03 respectively.

For each of these profiles the desalinization according to the column theory was calculated by use of the complete equation (*5*) with A = 21.0 and $2k$ = 5 cm. As an example the results for the sampling date October 5, 1945 (v = 1.95 ml. per sq. cm.) are given in table 3.

The theoretical curves obtained in this way are shown in figure 3B. Comparison of these curves with the experimental data reproduced in figure 3A shows that the theory gives—at least qualitatively—a good account of the observed changes.

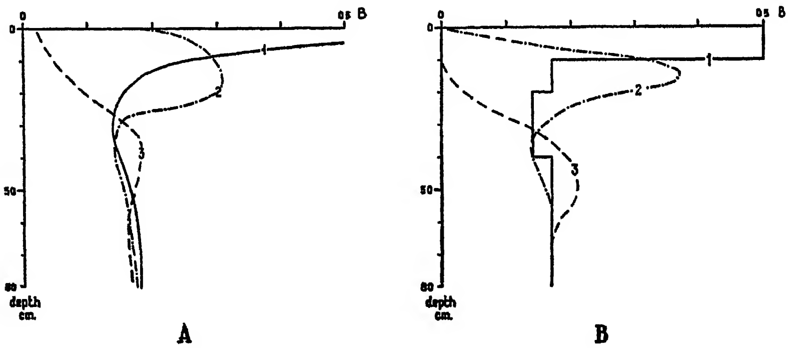

FIG. 3. DESALINIZATION ON SAMPLING SPOT SJ 1
Sampling dates: 1, August 23, 1945; 2, October 5, 1945; 3, March 12, 1945.
A: observed; B: calculated from equation (*5*) with A = 21.0; $2k$ = 5 cm.

TABLE 3

Calculation of the theoretical salinity-depth curve of the sampling spot SJ 1, October 5, 1945

Depth Below Soil Surface	Layer 0–80 cm. B_0 = 0.50	Layer 10–80 cm. B_0 = −0.33	Layer 20–80 cm. B_0 = −0.03	Layer 40–80 cm. B_0 = +0.03	Total
cm.					
5	0.12	—	—	—	0.12
10	0.30	—	—	—	0.30
15	0.45	−0.08	—	—	0.37
20	0.49	−0.20	—	—	0.29
25	0.50	−0.30	−0.01	—	0.19
30	0.50	−0.32	−0.02	—	0.16
35	0.50	−0.33	−0.03	—	0.14
40	0.50	−0.33	−0.03	—	0.14
45	0.50	−0.33	−0.03	+0.01	0.15
50	0.50	−0.33	−0.03	+0.02	0.16
55	0.50	−0.33	−0.03	+0.03	0.17

On closer observation, it appears, however, that the original variations in salt content have been blurred to a greater extent in practice than follows from theory; this difference may be due to the assumed value of $2k = 5$ cm. being too low for this profile.

SUMMARY AND CONCLUSIONS

The desalinization of soil profiles observed after the inundations of 1944–45 in the southwestern part of the Netherlands has been compared with the Glueckauf theory of column operation. In this comparison a good qualitative agreement between observations and theory has been found, even for nonhomogeneously saline profiles. Quantitatively, for light soils, the values of $\bar{v}$ predicted from the theory do not deviate more than 20 per cent from the observed values. In heavy soils, however, larger deviations occur as a result of the presence of cracks. The theoretical plate thickness—$2k$—in the profiles observed appeared to be approximately 5 cm.

The theory of column operation may also be applied to movements of other soil constituents which are not adsorbed by the soil particles, for example, the leaching of NO_3 ions. In this respect the theory may serve as a tool in fertilizer placement research.

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OCCURRENCE OF AZOTOBACTER IN CERTAIN WESTERN SOUTH CAROLINA SOILS

WILLIAM P. VanESELTINE

Clemson Agricultural College[1]

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The report by Peele and Wilson (5) that the Piedmont soils of South Carolina are strikingly deficient in legume bacteria (*Rhizobium* spp.) has stimulated interest in the distribution of other nitrogen-fixing organisms in these soils. During 1950–51 it was decided to begin investigation of the distribution in this region of the aerobic, nonsymbiotic, nitrogen-fixing bacteria *Azotobacter*. Except for inclusion of six South Carolina soil samples by Gainey (2) in his study of the influence of soil reaction upon *Azotobacter*, apparently no previous study of the organism in these soils has been made. Gainey found *Azotobacter* in only three of the six soils he examined.

METHODS

Ten soil samples were collected from each of five of South Carolina's westernmost counties. Efforts were made to sample the 10 most abundant soil types in each county and to have the samples well distributed over the county. Six of the 50 samples represented mountain soils; the remainder were from the Piedmont Plateau. Except for three samples taken from pastures, all were from cultivated fields, gardens, or orchards. Each sample consisted of several borings 6 inches deep made with sterile soil augers or trowels at random locations in a representative field. The borings were combined in a single sterile container, which remained unopened until tests for *Azotobacter* were made within a week after collection of the samples.

Presence of *Azotobacter* in the first 12 samples was tested by three methods: (*a*) Ashby's elective culture-liquid medium method as modified by Allen (1, pp. 55–56) to test three different energy sources; (*b*) Curie's selective culture-agar plate method as modified by Martin (4); and (*c*) Winogradsky's spontaneous culture-soil plaque method with five modifications as described by Wilson (7). When growth appeared on the nitrogen-free media (methods *a*, *b*) or on the soil plaques (method *c*), a small portion was suspended in dilute iodine solution and examined microscopically.

In the modified Ashby's medium, typical cultures in which *Azotobacter* appeared showed during the first few days an increasing turbidity accompanied by evolution of gas. Pellicle formation began usually on the third or fourth day,

[1] Present address: Department of Veterinary Hygiene, School of Veterinary Medicine, University of Georgia, Athens. Soil samples were collected, and all bacteriological work was done while author was on the staff of the department of botany and bacteriology, Clemson Agricultural College. Chemical analyses of soil samples were obtained, and material was prepared for publication after author joined the staff of the University of Georgia.

starting as a whitish, gelatinous ring near the walls of the flask and then rapidly extending to cover the entire surface. The films, at first grayish white, somewhat opaque, and rather dry and wrinkled, began to darken during the second week of incubation, eventually becoming dark brown to nearly black. Microscopic observation of the cells from such cultures revealed an overwhelming predominance of large, blunt or ovoid, rod-shaped cells 2.0 to 2.5 by 3.0 to 4.0 μ with some apparently dividing cells which appeared as large, paired cocci 2.0 to 2.5 μ in diameter. Such cultures, and the cells therefrom, corresponded closely to published descriptions of *Azotobacter chroococcum* and were considered to represent positive tests for the presence of *Azotobacter*. After being shaken with sterile sand, transfer of a bit of surface growth from representative cultures to plates of modified Ashby's medium solidified with agar resulted in numerous large, convex, grayish white, semitransparent, mucoid colonies from which the gram-negative nature of the large *Azotobacter* cells was demonstrated.

A few cultures showed less typical pellicles; they were thicker, more gelatinous, and did not darken so much. Microscopic examination revealed numerous *Azotobacter*-like cells, but these were mixed with greater numbers of other organisms (smaller rod-shaped bacteria, ciliated and flagellated protozoa, and higher fungi) than were observed in the more typical cultures. Since these numerous *Azotobacter*-like cells were indistinguishable from those found in the typical cultures, however, and since other flasks inoculated with portions of the same soil samples resulted in typical films, it seemed reasonable to consider these flasks also as positive for *Azotobacter*. Subculturing from representative cultures of this type resulted in colonies similar in every way to those obtained from the more typical cultures.

With the first 12 samples the agar plate method also gave consistently positive results, but the soil plaques sometimes failed to show growth of *Azotobacter*. The liquid medium method, being also simpler to perform, was used exclusively, therefore, for the remaining 38 samples.

Besides determining the mere presence or absence of *Azotobacter*, an effort was made also to determine the relative abundance of *Azotobacter* in the soil samples by inoculating a series of flasks of the modified Ashby's mannitol medium with varying quantities of soil, and to correlate the relative abundance of the organisms with several soil factors.[2]

RESULTS AND DISCUSSION

By use of the modified Ashby's liquid medium, the presence of *Azotobacter* was demonstrated in every one of the 50 soil samples regardless of whether

[2] For pH determinations, the author is indebted to Mrs. W. B. Aull, South Carolina Soil Research Laboratory, Clemson Agricultural College. The determinations were made with a Beckman pH meter using a suspension of one part soil in two parts distilled water. For determinations of organic matter and mineral elements, acknowledgment is made to Dr. Joel E. Giddens, department of agronomy, University of Georgia. Organic matter was determined by the modified chromic acid titration method described by Walkley and Black, *Soil Sci.* 37: 29–37 (1934). The nitrogen, phosphorus, potassium, calcium, and magnesium extractable with dilute $HCl \cdot H_2SO_4$ mixture were measured by standard methods in routine use in the department's soil testing laboratory.

TABLE 1

Abundance of Azotobacter in 50 soil samples from western South Carolina collected at different seasons and varying in soil type, pH, and content of mineral elements and organic matter

Samples and Variable Factors*	Samples Containing 40 or More *Azotobacter* per Gram of Soil		Samples Containing 20 or Fewer *Azotobacter* per Gram of Soil	
	Number	Per cent	Number	Per cent
21 fall samples (Sept., Oct., Nov., 1950)	14	66.7	7	33.3
7 winter samples (Dec., 1950, Jan., Feb., 1951)	2	28.6	5	71.4
22 spring samples (March, April, May, 1951)	3	13.6	19	86.4
7 sandy clay loams	5	71.4	2	28.6
18 sandy loams	8	44.5	10	55.5
7 clay loams	3	42.9	4	57.1
6 fine sandy loams	1	16.7	5	83.3
7 loams	1	14.3	6	85.7
5 alluvial soils	1	20.0	4	80.0
26 samples, pH 5.85 or higher	14	53.8	12	46.2
24 samples, pH less than 5.85	5	20.8	19	79.2
25 samples, CaO > 1,050 lb./A	14	56.0	11	44.0
24 samples, CaO < 1,050 lb./A	5	20.8	19	79.2
29 samples, MgO > 5 lb./A	13	44.8	16	55.2
20 samples, MgO = 5 lb./A	5	25.0	15	75.0
24 samples, P_2O_5 > 45 lb./A	11	45.8	13	54.2
25 samples, P_2O_5 < 45 lb./A	8	32.0	17	68.0
17 samples, NO_3 > 5 lb./A	7	41.2	10	58.8
32 samples, NO_3 = 5 lb./A	11	34.4	21	65.6
25 samples, K_2O > 125 lb./A	12	48.0	13	52.0
24 samples, K_2O < 125 lb./A	7	29.2	17	70.8
24 samples, organic matter >1.75%	8	33.3	16	66.7
25 samples, organic matter < 1.75%	11	44.0	14	56.0

* Season of year, soil type, and pH are known for all 50 samples, the other factors for only 49 samples.

mannitol, sodium benzoate, or ethyl alcohol was used as the energy source. Only Wilson (7, 8) in New York has previously reported *Azotobacter* in every soil examined, but a possible explanation of some workers' reports on the scarcity of these organisms might be found in the observation of Vandecaveye and Anderson (6) that *Azotobacter* was found in only 71 per cent of all soils they examined, but it was found in 94 per cent of the samples examined *immediately* after col-

lection. All *Azotobacter* tests reported herein were made within 1 week after collection of the soil samples.

As shown in table 1, the higher concentrations of *Azotobacter* were found most often in fall rather than in spring; in sandy clay loams and sandy loams rather than in loams or fine sandy loams; in soils of pH 5.85 or above rather than in more acid soils; and in the soils of higher calcium and magnesium content. Although the differences were less striking, higher *Azotobacter* concentrations were found slightly more frequently in the soils richer in phosphorus, nitrogen, and potassium. High *Azotobacter* concentrations were noted somewhat *less* frequently in the soils with the most organic matter content. Jensen (3) working with Danish soils similarly found no relation between density of *Azotobacter* and humus content of the soil.

Because of the large number of variable soil conditions (nine are considered in table 1), it was impossible to divide the soil samples into subgroups that would contain soils similar in all but one property, and consequently a rigid statistical treatment could not be used to decide which factors might be most important in controlling the numbers of *Azotobacter* in these soils.

CONCLUSIONS

It is concluded that: (*a*) the elective culture method using a modified Ashby's medium is satisfactory for detecting *Azotobacter* in these soils; (*b*) the *Azotobacter* are widely distributed, though perhaps not numerous, in the soils of western South Carolina; and (*c*) by materially increasing the number of samples tested, the methods used in this study can be made to yield information of value concerning the effect upon *Azotobacter* numbers of such factors as season of year, soil type, soil pH, and abundance of certain mineral elements in the soil.

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EFFECT OF SOIL-CONDITIONER-FERTILIZER INTERACTIONS ON SOIL STRUCTURE, PLANT GROWTH, AND YIELD

J. L. MORTENSEN AND W. P. MARTIN

Ohio Agricultural Experiment Station[1]

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A number of recent studies (1, 6, 8, 13, 22, 23) have indicated that synthetic polyelectrolytes are effective agents in stabilizing favorable physical properties of soil. Laws (10) found, however, that the presence of organic matter and 10 to 15 per cent clay, and the absence of free calcium carbonate, increased the effectiveness of soil conditioners. Martin and Aldrich (12) reported that the binding action of some conditioner materials was reduced by the presence of high ratios of exchangeable sodium and potassium. Jones[2] noted that, in general, hydroxyl and phosphate ions increased the effectiveness of conditioners, and that the effect of other anions depended somewhat upon the associated cation. Calcium and magnesium, except when added as the hydroxide, reduced the effectiveness of the conditioner.

Engibous[3] studied the effect of conditioner compounds on nutrient uptake in the greenhouse and concluded that the treatment had little effect upon phosphorus and potassium accumulation in rye grass. Increased accumulation of calcium and sodium was attributed to additions of these elements as components of conditioners. Bould and Tolhurst (4) reported an increase in the availability of phosphorus, as measured by the Neubauer method, in conditioner-treated soils. Fuller *et al.* (7) noted an increase in the nitrogen and phosphorus content of barley grain, hegari leaves, and cotton leaves and petioles as a result of conditioner treatment.

Yield increases due to conditioner treatment in the field have been noted by a number of investigators (1, 6, 8, 13, 14, 22), but such studies have also indicated that increased yields are not always associated with marked improvement in physical properties of soil.

This study was designed to determine the effect of two synthetic polyelectrolytes, including fertilizer interactions, on several physical properties of soil and on crop growth, composition, and yield, 1 and 2 years after application.

FIRST YEAR—CORN

Materials and methods

The experimental design was a randomized block factorial with four replicates, the nitrogen + phosphorus + potassium fertilization interaction being com-

[1] Contribution from the department of agronomy, Ohio State University and Ohio Agricultural Experiment Station. Journal Article 48-55. The junior author's address is now department of soil science, University of Minnesota.

[2] Jones, M. B., Ohio Agricultural Experiment Station. Unpublished data.

[3] Engibous, J. C. The effect of synthetic polyelectrolytes on some physical and biochemical properties of certain Ohio soils and upon yield and composition of plants. 1952. (Unpublished Doctoral dissertation, Ohio State University, Columbus.)

TABLE 1

Some chemical and physical properties of Hoytville silty clay

Readily soluble phosphorus . . . *lb./A.*	380
Exchangeable potassium . . . *lb./A.*	740
Cation-exchange capacity . . . *me./100 g.*	28
Organic matter . . . *per cent*	5.4
pH . . .	6.6
Moisture equivalent . . . *per cent*	31.0

pletely confounded. Plot size was 30 feet by 17½ feet (0.035 acre). The variables being tested were HPAN (hydrolyzed polyacrylonitrile) and VAMA (a mixture of calcium hydroxide and a copolymer of vinyl acetate and the partial methyl ester of maleic acid) conditioners, and nitrogen, phosphorus, and potassium fertilizers, with Ohio W65 corn the assay plant.

HPAN and VAMA in the powder form were applied on May 16, 1952, to the plowed soil surface of Hoytville silty clay (table 1) at the rate of 0.12 per cent, and thoroughly incorporated by disking. After the conditioners had been incorporated, the following fertilizers were broadcast: ammonium sulfate at the rate of 125 pounds N per acre to all nitrogen plots; 50 pounds P_2O_5 per acre as treble superphosphate to all phosphorus plots; and 50 pounds K_2O per acre as potassium chloride to all potassium plots. The equivalent of 250 pounds of 10–10–10 per acre was applied, where appropriate, in the row at the time of planting (May 31, 1952). Approximately 18,800 seed per acre were dropped in 42-inch rows.

A modified Yoder wet-sieving method (13) was used to determine the percentage of water-stable aggregates. Porosity measurements were conducted by the method of Leamer and Shaw (11), 40 cm. of tension being used. The moisture equivalent and water-holding capacity were determined by the centrifuge method of Briggs and McLane (5). Cation-exchange capacity determinations were made by the ammonium acetate method suggested by Peech *et al.* (17). Field moisture percentage (0 to 6 inches) was determined after a 24-hour drying period at 105° C. A soil-water ratio of 1:3 was used in determining pH by the glass electrode.

Corn leaf tissue for all plant analyses was obtained within a half-hour sampling period from the same position on each plant. Ten leaves from each plot were cut at the sheath, quick-frozen, and dried by lyophilization. A stretch of 25 feet of the three center rows of each plot was harvested by hand on October 20. Moisture content of the kernels was determined by oven-drying at 105°. Total nitrogen in the leaf tissue and grain was determined by the Kjeldahl procedure, phosphorus by the Shelton and Harper method (21), and potassium on neutral *N* ammonium acetate extracts by flame photometer according to the internal standard procedure.

Results and discussion

Analysis of soil. The total percentage of water-stable aggregates and percentage aeration porosity were significantly increased by conditioner treatment

TABLE 2

Aggregation (October 13) and aeration porosity (August 14) of Hoytville clay treated with fertilizers and 0.12 per cent HPAN and VAMA

Conditioner	Aggregation (Particles > 0.25 mm.)								
	Check	N	P	K	NP	NK	PK	NPK	Av.
	%*	%	%	%	%	%	%	%	%
Untreated	71	73	70	64	73	68	70	72	70
HPAN	78	73	81	86	80	81	77	81	82
VAMA	82	88	84	85	86	81	86	89	85
Average	77	78	78	78	80	77	78	81	79

LSD(0.05) between two fertilizer means.......................... .......N.S.
LSD(0.01) between two conditioner means..................... ..3 per cent
LSD(0.01) between two conditioner means for one fertilizer..... ..8 per cent
LSD(0.01) between two fertilizer means for a given conditioner. .11 per cent

Conditioner	Aeration Porosity								
	Check	N	P	K	NP	NK	PK	NPK	Av.
	%	%	%	%	%	%	%	%	%
Untreated	23	11	15	14	17	19	17	13	16
HPAN	24	19	19	14	20	19	22	15	19
VAMA	26	20	24	20	25	18	29	22	23
Average	24	17	19	16	21	19	23	17	19

LSD(0.05) between two fertilizer means.................................N.S.
LSD(0.01) between two conditioner means...............................2 per cent
LSD(0.05) between two conditioner means for one fertilizer..............N.S.
LSD(0.05) between two fertilizer means for a given conditioner...........N.S.

* Aggregation percentages, by weight.

(table 2). VAMA was more effective than HPAN. The highly significant conditioner-fertilizer interaction strongly suggests that conditioner effectiveness in stabilizing soil aggregates in the field is affected by presence of fertilizer salts. Amelioration of surface crusting and a friable structure were maintained throughout the growing season.

The moisture equivalent, water-holding capacity, and field moisture percentage of Hoytville silty clay were not altered by conditioner or fertilizer treatment in the field. Bodman and Hagan (3) and Peters *et al.* (18) also reported that available moisture was not altered by conditioner treatment in the field.

The cation-exchange capacity and pH of Hoytville silty clay were not altered by treatment with conditioners. The concentration of the conditioner materials was evidently too low to affect these properties.

Analysis of plants. The effect of soil structure on nutrient uptake and plant growth has been emphasized in a number of recent publications (16, 19). Use

TABLE 3

Effect of fertilizer and 0.12 per cent HPAN and VAMA treatments on nitrogen content of corn leaf tissue (August 14)

Conditioner	Nitrogen Content of Corn Leaf Tissue								
	Check	N	P	K	NP	NK	PK	NPK	Average
	%	%	%	%	%	%	%	%	%
Untreated	1.89	2.55	2.30	1.81	2.60	2.58	1.75	2.43	2.24
HPAN	1.72	2.76	1.51	2.53	2.53	2.38	1.79	2.39	2.08
VAMA	1.64	2.42	2.04	1.63	2.67	2.40	1.79	2.58	2.15
Average	1.75	2.58	1.95	1.66	2.60	2.45	1.78	2.47	2.16

LSD(0.01) between two fertilizer means...................... .0.45 per cent
LSD(0.01) between two conditioner means...................... .0.13 per cent
LSD(0.05) between two conditioner means for one fertilizer..... .0.26 per cent
LSD(0.05) between two fertilizer means for a given conditioner. .0.26 per cent

Mean responses for main effects and interactions

Fertilizer	Untreated	HPAN	VAMA
$\bar{N}$	+0.50**	+0.72**	+0.66**
$\bar{P}$	−0.01	+0.01	+0.16
$\bar{K}$	−0.22*	−0.04	−0.01
$\bar{N}\bar{P}$	+0.06	+0.03	+0.02
$\bar{N}\bar{K}$	+0.12	−0.05	−0.04
$\bar{P}\bar{K}$	+0.17	+0.09	−0.02

* Significant at 5 per cent level.
** Significant at 1 per cent level.

of soil conditioners in stabilizing desirable physical properties of soil has become a valuable tool for studying such relationships.

Leaf samples were taken three times during the growing season and the results, as affected by conditioner and fertilizer treatment, were in general agreement for all sampling dates. Seasonal alterations in the percentages of nitrogen, phosphorus, and potassium were similar to those reported by Sayre (20). Table 3 indicates that nitrogen fertilization was effective in significantly increasing the percentage of nitrogen in corn leaves. As an average of all fertilizer treatments, nitrogen content was significantly reduced by HPAN treatment, but in presence of nitrogen fertilizer, conditioner treatment significantly increased the nitrogen percentage of corn leaf tissue. As discussed later, plants growing in conditioner-treated plots matured earlier. The movement of nitrogen from leaf tissue to the developing ear (20) could partly account for the lower nitrogen content in leaf tissue of plants growing in conditioner-treated plots that did not receive nitrogen fertilization. Neither conditioner nor fertilizer treatment had any significant effect upon the accumulation of phosphorus (average = 0.21 per cent) and potassium (average = 1.9 per cent) in corn leaf tissue. The high

TABLE 4

Effect of fertilizer and 0.12 per cent HPAN and VAMA treatments on height of corn plants

Conditioner	Height of Corn Plants								
	Check	N	P	K	NP	NK	PK	NPK	Average
	in.	*in.*	*in.*	*in.*	*in.*	*in.*	*in.*	*in.*	*in.*
July 10									
Untreated	38	32	34	43	42	43	42	42	40
HPAN	38	42	40	38	45	47	46	44	43
VAMA	47	49	42	50	44	44	47	50	47
Average	41	41	39	44	44	45	45	45	43
August 14									
Untreated	85	82	79	88	79	91	85	90	85
HPAN	83	90	83	86	88	91	90	94	88
VAMA	87	89	88	90	87	92	90	95	90
Average	85	87	83	88	85	91	88	93	68
September 19									
Untreated	84	83	82	87	86	92	85	87	86
HPAN	82	86	85	88	89	90	91	92	88
VAMA	86	89	89	89	89	94	91	94	90
Average	84	86	85	88	88	92	89	91	88

level of available phosphorus and potassium in Hoytville silty clay could account for the lack of significant differences in accumulation of these elements.

One of the most striking differences noted in the corn plants throughout the growing season was that in height. Table 4 indicates that plants growing in conditioner-treated and nitrogen-fertilized plots were consistently taller throughout the growing season. Throughout the growing season, ears on plants in the conditioner-treated plots, especially in combination with nitrogen fertilization, were larger and more fully developed.

In general, observations throughout the growing season substantiated the foregoing relationships. In growth and general appearance, corn plants in conditioner-treated and nitrogen-fertilized plots were superior to plants on other plots. During rather severe drouth periods (rainfall June through October was 10.8 inches), corn plants in plots that did not receive conditioner treatment wilted and leaf-rolled markedly. When soil samples were obtained for analysis, a more extensive root system was observed in conditioner-treated plots. Even though conditioner treatment apparently did not alter the wilting coefficient or field capacity of Hoytville silty clay, the "physiological availability" of water

TABLE 5

Effect of fertilizer and 0.12 per cent HPAN and VAMA treatments on moisture content of corn grain

Conditioner	Moisture Content of Corn Grain								
	Check	N	P	K	NP	NK	PK	NPK	Average
	%	%	%	%	%	%	%	%	%
Untreated	31.1	28.4	32.1	32.1	27.9	27.2	29.9	28.8	29.6
HPAN	28.7	25.7	28.6	27.9	27.2	26.8	29.1	27.3	27.5
VAMA	28.2	25.3	27.5	27.4	25.1	25.8	28.4	25.6	26.7
Average	29.3	26.5	29.4	28.8	26.4	26.6	29.1	27.2	27.9

LSD(0.01) between two fertilizer means........................ .2.4 per cent
LSD(0.01) between two conditioner means...................... .1.0 per cent
LSD(0.05) between two conditioner means for one fertilizer..... .N.S.
LSD(0.05) between two fertilizer means for a given conditioner. .N.S.

Mean responses for main effects and interactions

Fertilizer	Untreated	HPAN	VAMA
$\bar{N}$	−3.0**	−2.0**	−2.5**
$\bar{P}$	+0.2	+0.5	0.0
$\bar{K}$	−0.6	+0.5	+0.3
$\bar{N}\bar{P}$	+0.3	0.0	−0.2
$\bar{N}\bar{K}$	+0.5	+0.6	+0.2
$\bar{P}\bar{K}$	−0.1	+0.3	+0.4

** Significant at 1 per cent level.

between these values was evidently increased. This could have been a result of the stabilization of a more desirable aerobic environment in which energy requirements for water absorption would be affected or a result of the more extensive root systems that developed in treated plots, or both.

Yield and composition of grain. Table 5 indicates that grain harvested from conditioner-treated and nitrogen-fertilized plots contained significantly less moisture than grain from plots that did not receive these amendments. This would also indicate that a more rapid maturity resulted from conditioner treatment.

Nitrogen fertilization increased the nitrogen content of the grain (table 6). In addition, by a significant interaction which took place between fertilization and conditioner treatment, the nitrogen content of the grain was further increased. Neither conditioner treatment nor fertilization, however, significantly affected the percentage of phosphorus (average = 0.32 per cent) and potassium (average = 0.46 per cent) in the corn grain.

The yield data (table 7) indicate a significant increase in corn yield as a result of both conditioner and fertilizer treatment, with the nitrogen fertilization especially effective. The conditioner-fertilizer interaction in increasing yield

TABLE 6

Effect of fertilizer and 0.12 per cent HPAN and VAMA treatments on nitrogen content of corn grain

Conditioner	Nitrogen Content of Corn Grain								
	Check	N	P	K	NP	NK	PK	NPK	Average
	%	%	%	%	%	%	%	%	%
Untreated	1.37	1.65	1.30	1.43	1.59	1.55	1.38	1.55	1.48
HPAN	1.25	2.49	1.07	1.30	1.62	1.61	1.33	1.67	1.42
VAMA	1.33	1.67	1.26	1.23	1.60	1.53	1.22	1.65	1.44
Average	1.32	1.60	1.21	1.32	1.60	1.61	1.31	1.62	1.45

LSD(0.01) between two fertilizer means........... ....0.26 per cent
LSD(0.05) between two conditioner means...........................N.S.
LSD(0.05) between two conditioner means for one fertilizer............0.15 per cent
LSD(0.05) between two fertilizer means for a given conditioner........0.15 per cent

Mean responses for main effects and interactions

Fertilizer	Untreated	HPAN	VAMA
$\bar{N}$	+0.22**	+0.36**	+0.35**
$\bar{P}$	−0.04	0.00	0.00
$\bar{K}$	−0.01	−0.12	−0.06
$\bar{N}\bar{P}$	+0.02	+0.08	+0.03
$\bar{N}\bar{K}$	+0.08	+0.03	+0.01
$\bar{P}\bar{K}$	+0.02	+0.04	+0.07

** Significant at 1 per cent level.

was highly significant. Although no significant differences were noted in stand counts, conditioner treatment and nitrogen fertilization significantly increased the average weight per ear and the total number of ears produced. These treatments evidently also enhanced ear formation.

SECOND YEAR—OATS

To determine the effectiveness of conditioner and fertilizer treatment 1 year after application, the corn plots were used a year later in the following experiment with oats.

Materials and methods

After the corn harvest, all plots were thoroughly disked, and, then, just prior to planting they were disked again. On April 7, 1953, 2 bushels of Clinton 59 oats was seeded per acre and, at the same time, 400 pounds of 4–16–16 per acre was applied with a grain drill.

Soil and plant samples were taken and analyzed in a manner similar to that described for the corn experiment. Plants were sampled in the dough stage of the grain, 20 plants being obtained from each plot (April to July rainfall equaled 11.97 inches).

TABLE 7

Effect of fertilizer and 0.12 per cent HPAN and VAMA treatments on yield of corn

Conditioner	Yield of Corn†								
	Check	N	P	K	NP	NK	PK	NPK	Average
	bu.	*bu.*	*bu.*	*bu.*	*bu.*	*bu.*	*bu.*	*bu.*	*bu.*
Untreated	68	97	65	72	100	105	76	86	84
HPAN	72	103	74	82	108	112	68	110	91
VAMA	75	104	78	84	106	118	79	116	95
Average	72	101	72	79	105	112	74	104	90

LSD(0.01) between two fertilizer means..................... .21 bushels
LSD(0.05) between two conditioner means...................... ..4 bushels
LSD(0.01) between two conditioner means for one fertilizer..... .16 bushels
LSD(0.01) between two fertilizer means for a given conditioner. .24 bushels

Mean responses for main effects and interactions

Fertilizer	Untreated	HPAN	VAMA
$\bar{N}$	+27**	+34**	+32**
$\bar{P}$	−4	−2	0
$\bar{K}$	+2	+2	+9**
$\bar{N}\bar{P}$	−4	+2	+1
$\bar{N}\bar{K}$	−5	+1	+3
$\bar{P}\bar{K}$	−4	−3	−3

** Significant at 1 per cent level.
† Per acre; at 15.5 per cent moisture.

Borders were mowed from all plots and standing center strips were harvested with a self-propelled combine on July 18. A 5-minute waiting period after work with each plot was allowed to ensure complete removal of grain from the combine.

Results and discussion

Analysis of soil. Results of the wet-sieve analysis for aggregate stability, summarized in table 8, show that increased aggregation as a result of conditioner treatment was significantly maintained for a year. All values for this sampling date (May 2, 1953) are approximately 10 per cent lower than those of the previous season. It must be emphasized, however, that the empirical nature of the wet-sieving method, and the effect of moisture and tillage operations on aggregate stability, prevent a quantitative comparison of aggregation data between seasonal sampling dates. The fertilizer-conditioner interaction, which altered the state of aggregation the previous year, was not apparent at this later sampling date.

During seedbed preparation, it was noted that the soil mass around old corn

TABLE 8

Aggregation of Hoytville silty clay treated with fertilizers and 0.12 per cent HPAN and VAMA

Date of treatment May 16, 1952; date of sampling May 2, 1953

Conditioner	Particles > 25 mm.								
	Check	N	P	K	NP	NK	PK	NPK	Average
	%*	%	%	%	%	%	%	%	%
Untreated	60	57	60	64	61	63	59	60	61
HPAN	71	70	69	72	61	65	72	72	69
VAMA	80	72	73	75	80	75	74	78	76
Average	70	66	67	70	67	68	68	70	69

LSD(0.05) between two fertilizer means....................................N.S.
LSD(0.01) between two conditioner means................................5 per cent
LSD(0.05) between two conditioner means for one fertilizer...............N.S.
LSD(0.05) between two fertilizer means for a given conditioner...........N.S.

* Percentages, by weight.

TABLE 9

Effect of fertilizer and 0.12 per cent HPAN and VAMA treatments on nitrogen content of mature oat plants

Date of treatment May 16, 1952

Conditioner	Nitrogen Contents of Oat Plant Tissue								
	Check	N	P	K	NP	NK	PK	NPK	Average
	%	%	%	%	%	%	%	%	%
Untreated	1.32	1.65	1.16	1.24	1.62	1.66	1.32	1.64	1.45
HPAN	1.17	1.59	1.22	1.17	1.69	1.63	1.34	1.45	1.41
VAMA	1.05	1.55	1.17	1.02	1.45	1.58	1.19	1.55	1.32
Average	1.18	1.60	1.18	1.14	1.59	1.62	1.28	1.55	1.39

LSD(0.01) between two fertilizer means........................ .0.18 per cent
LSD(0.01) between two conditioner means...................... .0.10 per cent
LSD(0.05) between two conditioner means for one fertilizer..... .N.S.
LSD(0.05) between two fertilizer means for a given conditioner. .N.S.

Mean responses for main effects and interactions

Fertilizer	Untreated	HPAN	VAMA
$\bar{N}$	+0.38**	+0.33**	+0.41**
$\bar{P}$	0.00	+0.07	0.00
$\bar{K}$	+0.02	0.00	+0.02
$\bar{N}\bar{P}$	+0.08	−0.10*	−0.07
$\bar{N}\bar{K}$	−0.05	−0.09*	−0.02
$\bar{P}\bar{K}$	+0.05	−0.05	+0.05

* Significant at 5 per cent level.
** Significant at 1 per cent level.

TABLE 10

Effect of fertilizer and 0.12 per cent HPAN and VAMA treatments on phosphorus content of mature oat plants

Date of treatment May 16, 1952

Conditioner	Phosphorus Content of Oat Plant Tissue								
	Check	N	P	K	NP	NK	PK	NPK	Average
	%	%	%	%	%	%	%	%	%
Untreated	0.30	0.26	0.29	0.30	0.27	0.27	0.33	0.27	0.29
HPAN	0.31	0.25	0.33	0.32	0.28	0.28	0.34	0.28	0.30
VAMA	0.30	0.28	0.29	0.36	0.28	0.27	0.35	0.31	0.31
Average	0.30	0.26	0.30	0.33	0.28	0.27	0.34	0.29	0.30

LSD(0.01) between two fertilizer means..............................0.04 per cent
LSD(0.05) between two conditioner means............................0.01 per cent
LSD(0.05) between two conditioner means for one fertilizer............0.04 per cent
LSD(0.05) between two fertilizer means for one conditioner............0.04 per cent

Mean responses for main effects and interactions

Fertilizer	Untreated	HPAN	VAMA
$\bar{N}$	−0.04**	−0.05**	−0.04**
$\bar{P}$	+0.01	+0.02	0.00
$\bar{K}$	+0.02	+0.01	+0.03
$\bar{N}\bar{P}$	−0.01	−0.01	+0.01
$\bar{N}\bar{K}$	−0.01	0.00	−0.03*
$\bar{P}\bar{K}$	+0.01	−0.01	+0.01

* Significant at 5 per cent level.
** Significant at 1 per cent level.

roots was more easily broken off in conditioner-treated plots. In untreated plots, the large masses of soil which were retained on roots caused considerable difficulty in the drilling operation. Differences in appearance of the soil surface were less noticeable than during the previous year. Considerable slaking had taken place in all plots.

Analysis of plants. The effect of conditioner and fertilizer treatment on the percentage of nitrogen in mature oat plants is shown in table 9. Obviously the nitrogen content of oat plant tissue was significantly increased by the 1952 nitrogen fertilization, and plants growing in plots treated with conditioner contained significantly less nitrogen than did plants from untreated plots. These analyses confirmed visible differences in the growing plants. It is suggested that because of better structure and drainage, a probable increase in microbial activity[3] (15) and greater nitrate losses through leaching might account for loss of nitrogen in the soil, and consequently a decrease in nitrogen assimilation on conditioner-treated plots. As a result of increased microbial activity in conditioner-treated soils, the old corn stalks undoubtedly decomposed more rapidly, with a concomitant immobilization of nitrogen.

TABLE 11

Effect of fertilizer and 0.12 per cent HPAN and VAMA treatments on nitrogen content of oat grain

Date of treatment May 16, 1952

Conditioner	Nitrogen Content of Oat Grain								
	Check	N	P	K	NP	NK	PK	NPK	Average
	%	%	%	%	%	%	%	%	%
Untreated	2.03	2.38	2.05	2.02	2.19	2.27	1.93	2.34	2.15
HPAN	1.94	2.36	1.96	2.03	2.33	2.14	1.98	2.35	2.14
VAMA	1.84	2.16	2.08	1.95	2.26	2.17	2.15	2.35	2.12
Average	1.94	2.30	2.03	2.00	2.26	2.19	2.02	2.35	2.14

LSD(0.01) between two fertilizer means........................	.0.14 per cent
LSD(0.05) between two conditioner means......................	.N.S.
LSD(0.05) between two conditioner means and one fertilizer....	.0.19 per cent
LSD(0.05) between two fertilizer means and a given conditioner.	.0.15 per cent

Mean responses for main effects and interactions

Fertilizers	Untreated	HPAN	VAMA
$\bar{N}$	+0.29**	+0.34**	+0.24**
$\bar{P}$	−0.05	+0.04	+0.18
$\bar{K}$	+0.03	+0.03	+0.08
$\bar{N}\bar{P}$	0.00	+0.07	−0.05
$\bar{N}\bar{K}$	+0.02	−0.07	−0.04
$\bar{P}\bar{K}$	+0.06	+0.01	0.00

** Significant at 1 per cent level.

Phosphorus accumulation in mature oat plants was significantly increased by conditioner treatment and significantly decreased by the 1952 nitrogen fertilization, the conditioner-nitrogen interaction also being significant (table 10). As Arnon (2) has shown, absorption of phosphate by barley plants is hindered by competition with the rapidly absorbable nitrate ion. The likely higher nitrate content in nitrogen-fertilized plots could, therefore, account for the depression in phosphorus accumulation noted in this study.

Yield and composition of grain. Table 11 indicates that the 1952 nitrogen fertilization significantly increased the nitrogen content of oat grain. Conditioner treatment had little effect, but the nitrogen content of oat grain was significantly affected by the fertilizer-conditioner interaction. There were no significant differences in phosphorus (average = 0.39 per cent) or potassium (average = 0.66 per cent) accumulation in oat grain as a result of conditioner and fertilizer treatment.

Yields on the 1952 nitrogen-fertilized plots were increased by as much as 20 bushels per acre, but phosphorus and potassium fertilization had little effect on yield of oats on Hoytville silty clay (table 12). Conditioner treatment caused

TABLE 12

Effect of fertilizer and 0.12 per cent HPAN and VAMA treatments on yield of oats

Date of treatment May 16, 1952

Conditioner	Yield of Oats†								
	Check	N	P	K	NP	NK	PK	NPK	Average
	bu	*bu.*	*bu.*	*bu.*	*bu.*	*bu.*	*bu.*	*bu.*	*bu.*
Untreated	58	79	55	62	69	78	51	77	66
HPAN	51	81	51	62	78	70	52	63	64
VAMA	58	69	48	56	78	71	42	67	61
Average	56	76	51	60	75	73	48	69	64

LSD(0.01) between two fertilizer means....................... .12 bushels
LSD(0.05) between two conditioner means...................... .N.S.
LSD(0.05) between two conditioner means for one fertilizer..... .N.S.
LSD(0.05) between two fertilizer means for a given conditioner. .N.S.

Mean responses for main effects and interactions

Fertilizer	Untreated	HPAN	VAMA
$\bar{N}$	+19**	+19**	+20**
$\bar{P}$	−6*	−5	−5
$\bar{K}$	+2	−3	−4
$\bar{N}\bar{P}$	+1	0	+7*
$\bar{N}\bar{K}$	+2	−10**	−1
$\bar{P}\bar{K}$	0	−3	−6

* Significant at 5 per cent level.
** Significant at 1 per cent level.
† Per acre; at 15.5 per cent moisture.

an insignificant decrease in yield, the result undoubtedly of the decreased nitrogen assimilation noted earlier. Oat yield was significantly decreased by 1952 phosphorus fertilization on untreated plots and by nitrogen-potassium fertilization on HPAN-treated plots.

SUMMARY

Field application of the synthetic polyelectrolytes HPAN and VAMA markedly influenced the physical properties of Hoytville silty clay as evidenced by a significant increase in aggregate stability and aeration porosity. Although conditioner-treated plots appeared to dry out more rapidly after rainstorms, the field-moisture percentage, water-holding capacity, and moisture equivalent were not altered by either conditioner or fertilizer treatment. Cation-exchange capacity and pH were not altered by treatment.

Throughout a second growing season, improved soil structure and stability of aggregates as a result of conditioner treatment were significantly maintained. Aggregation values for all plots, treated and untreated, were approximately 10 per cent less than the values obtained 1 year previously.

Accumulation of nitrogen in corn leaf tissue and corn grain was significantly increased by nitrogen fertilization, but it was decreased by conditioner treatment in absence of nitrogen fertilization. Fertilizer and conditioner treatment had little effect on phosphorus and potassium accumulation because of the large quantities of these elements in Hoytville silty clay. Growth measurements of corn throughout the growing season indicated, in addition to lower moisture percentage in corn grain, that conditioner treatment and nitrogen fertilization significantly increased the rate of growth and maturation of corn. Corn plants growing in conditioner-treated plots, especially in combination with nitrogen fertilization, were greener, more vigorous, larger, and exhibited very little wilting during drouth periods. It is suggested that conditioner treatment increased the "physiological availability" of water in Hoytville silty clay. Yield of corn was significantly increased by nitrogen fertilization and conditioner treatment.

The 1952 nitrogen fertilization markedly increased nitrogen content of mature oat plants and oat grain and yield of oats the second year of this experiment. Conditioner treatment significantly reduced nitrogen content of oat tissues but had little effect on yield. A probable increase in the rate of nitrification and larger nitrate losses in conditioner-treated plots could account for this observed reduction of nitrogen content.

The significant effect of the fertilizer-conditioner interactions in altering the state of aggregation, in increasing nitrogen content of leaf tissue and grain of corn, and in increasing the rate of growth and yield of corn the first year of this study suggests that the effectiveness of conditioner materials was altered by presence of fertilizer salts or that the effectiveness of fertilizer was influenced by certain physical properties of the Hoytville silty clay stabilized by conditioner treatment. The analysis of variance for mean responses for main effects and interactions indicated that the effectiveness of nitrogen fertilization in increasing corn and oat yields was significantly increased by conditioner treatment.

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VERTICAL DISTRIBUTION OF NITROGEN, PHOSPHORUS, AND POTASSIUM IN SOME SOILS OF EAST PAKISTAN

A. KARIM AND D. H. KHAN

Dacca University, East Pakistan

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Literature on the profile distribution of the different forms of nitrogen, phosphorus, and potassium and its bearing on pedogenic characteristics is very scanty. During recent years, Mattson *et al.* (13) have studied the course of translocation of different forms of phosphorus in some major soil groups of Sweden, but corresponding information on potassium and nitrogen in soils is meager.

The purpose of the present investigation was to study the vertical distribution of the different forms of nitrogen, phosphorus, and potassium; the interrelationships of these forms; and their bearing on pedogenic characteristics of some gray-brown podzolic soils of East Pakistan.

MATERIALS AND METHODS

Soils selected were sampled from an area 20 miles east of Dacca, the capital of East Pakistan. The area represents a highland arc with conspicuous crests and troughs, having a Prescott ratio for soil boundaries of 17.16, Meyer's N.S.Q. of 287.77, and Lang's rain factor of 72.76. The soils under investigation belong to the gray-brown podzolic group. The vegetation association comprises, for the most part, rice—Oryza sativa (L); jute—*Corchorus* spp.; common bean—*Phaseolus vulgaris* (L); and native grass.

The soil types collected from the area were tentatively named after their surface color and texture as follows:

Soil types		*Location and vegetation*
Brownish gray fine sandy loam	(bG FSL)	Crest soils under native grass cover.
Dark gray fine sandy loam	(DG FSL)	
Gray fine sandy loam/1	(G FSL/1)	Crest soils under cultivation to such crops as common bean and jute.
Gray fine sandy loam/2	(G FSL/2)	
Grayish yellow fine sandy loam	(gY FSL)	Trough soils under cultivation to paddies.
Yellowish gray fine sandy loam	(yG FSL)	

Because of the wide occurrence of gray fine sandy loam in the area surveyed, two types were sampled.

In general, the agricultural productivity of the area under investigation is deteriorating. The crest soils under common bean and jute cover (G FSL/1 and G FSL/2) exhibit very poor crop growth. The trough soils (gY FSL and yG FSL), which have been producing rice for a long time, also exhibit poor crop growth. The native grass vegetation on the crest soils (bG FSL and DG FSL) is of medium to poor growth.

Laboratory analyses of the samples, collected on a strictly horizon basis,

were made for the different forms of nitrogen, phosphorus, and potassium and also for organic carbon, free Fe_2O_3, loss on acid treatment, cation-exchange capacity, and SiO_2–R_2O_3 ratio of the clay fractions corresponding to the soil samples.

Total ammonia and nitrate N were determined by the method of Piper (15). Organic N was obtained indirectly by deducting inorganic N (NH_4 and NO_3) from total N.

Inorganic (0.2 N H_2SO_4-soluble), organic, sesquioxide-bound (acid oxalate-soluble), and aluminum-bound P (2.5 per cent CH_3COOH-soluble) were determined according to Mattson *et al.* (13). Available P (0.002 N H_2SO_4-soluble) was determined by Truog's (20) method as modified by Lynch *et al.* (11). Adsorbed P was determined by Piper's (15) NaOH displacement method. Iron-bound P was obtained by subtracting Al-bound P from R_2O_3-bound P.

Total and adsorbed K_2O were determined according to Piper (15). Available K_2O was obtained by Dyer's citric acid-extraction method. Fixed K_2O in soil and clay was determined by subtracting available and adsorbed K_2O from the total K_2O in soil and clay respectively. Fixed K_2O in noncolloid was obtained indirectly by deducting fixed K_2O in clay from fixed K_2O in soil.

Loss on acid treatment, total cation-exchange capacity, organic carbon, and SiO_2–R_2O_3 were determined according to Piper (15). Free Fe_2O_3 was determined by Karim's (8) nascent hydrogen reduction method.

DISTRIBUTION OF DIFFERENT FORMS OF NITROGEN

The vertical distribution of organic, ammonia, and nitrate nitrogen in the soil profiles is shown in table 1.

Organic N

Organic N constituted the bulk of the total nitrogen in the soils. This form of N, which may be considered to be a direct reflection of humic nitrogen, showed a gradual decrease with depth and no tendency to accumulate in the B horizons. It was closely related to organic carbon.

Ammonia and nitrate N

The ammonia and nitrate N contents of the soils under investigation were very low. They showed no regularity in distribution down the profiles. Ammonia N showed a surface accumulation in bG FSL, G FSL/2, gY FSL, and yG FSL; and nitrate N, a surface deposition in DG FSL, G FSL/2, and yG FSL.

DISTRIBUTION OF DIFFERENT FORMS OF PHOSPHORUS

The available, inorganic, organic, sesquioxide-bound, Fe-bound, Al-bound, and adsorbed P determined in the soils are shown in tables 2 and 3.

Available P

The 0.002N H_2SO_4-soluble P which, according to Truog (20) and Lynch *et al.* (11), has been assumed to be available to plants, showed an accumulation in the B_1 horizons of DG FSL, G FSL/1, and G FSL/2. The general level of available

TABLE 1

Distribution of different forms of nitrogen in soils

Soil Type	Horizon	Depth	Total N	Organic N	Ammonia N	Nitrate N
		in.	%	%	%	%
bG FSL	A_{1a}	0–1	0.143	0.140	0.0017	0.0008
	A_{1b}	1½–2½	0.126	0.122	0.0018	0.0018
	B_1	4–7	0.101	0.098	0.0001	0.0025
	B_2	10–17	0.073	0.070	0.0014	0.0013
	B_3	20–35	0.037	0.035	0.0010	0.0008
DG FSL	A_{1a}	0–¾	0.168	0.164	0.0014	0.0025
	A_{1b}	1½–3½	0.081	0.078	0.0009	0.0023
	B_1	4½–7½	0.070	0.067	0.0018	0.0014
	B_2	9½–24	0.047	0.044	0.0015	0.0013
	B_3	28–46	0.032	0.028	0.0028	0.0013
G FSL/1	A	0–2	0.132	0.129	0.0012	0.0013
	B_1	4–7	0.080	0.077	0.0016	0.0017
	B_2	9–18	0.063	0.061	0.0008	0.0008
	B_3	22–36	0.056	0.054	0.0015	0.0002
G FSL/2	A	0–1½	0.096	0.093	0.0018	0.0009
	B_1	3–8	0.083	0.081	0.0014	0.0001
	B_2	10–20	0.063	0.061	0.0008	0.0010
	B_3	23–37	0.053	0.051	0.0007	0.0008
gY FSL	A	0–3	0.084	0.080	0.0020	0.0015
	B_1	4½–14	0.087	0.084	· 0.0007	0.0018
	B_2	16½–29	0.087	0.083	0.0022	0.0013
	B_3	32–43	0.082	0.079	0.0009	0.0016
yG FSL	A	0–3	0.105	0.101	0.0021	0.0019
	B_1	4½–7	0.063	0.060	0.0013	0.0016
	B_2	10–25	0.064	0.061	0.0014	0.0013
	B_3	27–36	0.052	0.049	0.0022	0.0010

P was much higher in G FSL/1 and G FSL/2 than in the other soils. This form averaged about 20 per cent of the total phosphorus in contrast to about 5 per cent in the other soils (table 3).

Inorganic P

Inorganic P had accumulated in the B_1 horizons of DG FSL, G FSL/1, G FSL/2, and gY FSL. This finding is in agreement with that of Mattson *et al.* (13), who found an accumulation of 0.2 N H_2SO_4-soluble P in the B horizon of some podzolic soils of Sweden. The inorganic phosphorus content of G FSL/1 and G FSL/2 was much greater than that of the other soils.

Organic P

Organic P showed a subsurface accumulation in all soils except yG FSL. This

TABLE 2

Distribution of different forms of phosphorus in soils

Expressed as mg. per 100 g. soil

Soil Type	Horizon*	Available P	Inorganic P	Organic P	R_2O_3-P	Fe-P	Al-P	Adsorbed P	Total P
bG FSL	A_{1a}	1.92	1.59	2.69	0.97	0.88	0.09	1.15	39.60
	A_{1b}	1.02	1.81	1.75	4.15	4.08	0.06	1.25	40.12
	B_1	1.03	1.45	9.06	1.89	1.85	0.05	1.33	42.67
	B_2	0.92	1.21	12.98	0.33	0.22	0.10	1.25	30.33
	B_3	0.80	1.15	12.97	3.79	3.74	0.05	1.18	27.84
DG FSL	A_{1a}	1.06	5.99	17.19	8.05	7.85	0.20	1.90	38.78
	A_{1b}	1.06	8.09	12.60	7.94	7.84	0.10	2.36	36.80
	B_1	2.68	11.08	23.00	17.62	17.42	0.20	4.58	42.01
	B_2	1.58	8.27	10.94	8.34	8.23	0.11	3.13	35.76
	B_3	0.82	3.86	8.20	3.68	3.58	0.10	1.10	35.55
G FSL/1	A	6.83	25.53	6.71	8.01	5.97	2.04	8.80	32.54
	B_1	19.55	69.60	8.71	13.04	3.39	9.65	17.79	80.62
	B_2	11.62	29.71	14.85	12.79	9.83	2.97	10.67	57.88
	B_3	3.52	9.16	10.37	8.96	8.73	0.23	15.60	38.56
G FSL/2	A	3.38	23.60	5.20	8.29	7.76	5.36	6.83	34.11
	B_1	12.12	37.55	4.65	13.81	9.05	4.27	8.30	52.45
	B_2	9.21	37.88	3.65	11.82	9.68	2.13	8.25	52.18
	B_3	3.29	8.62	6.31	6.76	6.48	0.27	4.03	23.52
gY FSL	A	2.28	4.33	7.79	1.36	1.26	0.10	2.05	20.87
	B_1	1.89	4.99	8.97	3.16	3.09	0.07	1.94	22.20
	B_2	1.30	6.27	14.93	2.76	2.64	0.12	2.67	27.13
	B_3	1.23	10.17	17.21	4.21	4.12	0.08	2.62	32.03
yG FSL	A	0.98	10.08	11.94	2.78	2.67	0.11	2.23	22.23
	B_1	0.84	2.38	10.78	1.33	1.25	0.08	1.07	18.01
	B_2	0.74	1.58	7.71	1.99	1.94	0.05	1.24	15.95
	B_3	0.76	1.62	7.77	4.50	4.45	0.06	1.33	18.16

* See table 1 for depths.

The relation of organic P to organic C and organic N is shown in table 4. The ratios C/N, C/P, and N/P show that the rate of breakdown and disappearance of organic P with increasing depth is much less than is that of organic C. A similar observation was made by Ghani and Aleem (5) and Thompson and Black (19).

From a consideration of the breakdown of organic C, organic N, and organic P and their consequent mineralization, various workers have determined the C/P and N/P ratios of soils. In a study of 24 samples of surface soils from Ohio, Schollenberger (17) found the average ratio of N to organic P to be 10.0. Pearson and Simonson (14), from a study of vertical distribution of organic P, N, and C in seven Iowa soil profiles, found the average ratios of C/P and N/P to be 116 and 11.2 respectively. Kaila (7), likewise, reported definite correlations for organic P,

TABLE 3

Percentages of different forms of phosphorus in soils*

Soil Type	Horizon†	Available P	Inorganic P	Organic P	R_2O_3-P	Fe-P	Al-P	Adsorbed P
		%	%	%	%	%	%	%
bG FSL	A_{1a}	4.8	4.0	6.8	2.4	2.2	0.2	2.9
	A_{1b}	2.6	4.5	4.4	10.3	10.2	0.2	3.1
	B_1	2.4	3.4	21.2	4.4	4.3	0.1	3.1
	B_2	3.0	4.0	42.8	1.1	0.7	0.3	4.1
	B_3	2.9	4.1	46.6	13.6	13.4	0.2	4.2
DG FSL	A_{1a}	2.7	15.4	44.3	20.7	20.2	0.5	5.0
	A_{1b}	2.9	21.9	34.2	21.6	21.3	0.3	6.4
	B_1	6.4	26.4	54.7	41.9	41.5	0.5	10.9
	B_2	4.4	23.1	30.6	23.3	23.0	0.3	8.8
	B_3	2.3	10.8	23.1	10.3	10.1	0.3	3.3
G FSL/1	A	21.0	78.5	20.6	24.6	18.3	6.3	27.3
	B_1	24.2	86.3	10.8	16.2	4.2	12.0	22.1
	B_2	20.1	51.3	25.6	22.1	16.9	5.1	18.5
	B_3	9.1	23.8	26.9	23.3	22.7	0.6	13.8
G FSL/2	A	9.9	69.2	15.3	24.3	22.7	1.6	20.1
	B_1	23.1	71.6	8.8	25.4	17.2	8.1	15.8
	B_2	17.6	72.6	7.0	22.7	18.6	4.1	16.6
	B_3	14.0	36.7	26.8	28.7	27.6	1.2	17.1
gY FSL	A	10.9	20.7	37.3	6.5	6.0	0.5	9.8
	B_1	8.5	22.5	40.4	14.2	13.9	0.3	8.3
	B_2	4.8	23.1	55.0	10.2	9.7	0.5	9.8
	B_3	3.8	31.8	53.7	13.1	12.5	0.3	8.2
yG FSL	A	4.4	45.4	53.7	12.5	12.0	0.5	10.5
	B_1	4.7	13.2	59.8	7.4	6.9	0.4	5.9
	B_2	4.6	9.9	48.4	12.5	12.2	0.3	7.8
	B_3	4.2	8.9	42.2	24.8	24.5	0.3	7.3

* Computed as percentages of total phosphorus.
† See table 1 for depths.

C, and N; the average ratios of C/P and N/P in 70 samples of mineral soils were found to be 130 and 8.4 respectively. Ghani and Aleem (5), however, found very little relationship between the amounts of organic C and organic P, the average C/P ratio being 51, which is much less than the ratios reported by other workers. The average ratios of C/P and N/P for the soils in the present investigation, 122 and 11.80 respectively, are in close agreement with those of Schollenberger (17), Pearson and Simonson (14), and Kaila (7).

Sesquioxide-bound P

The acid-oxalate-soluble P, which has been regarded as R_2O_3-bound P, showed a deposition in the B horizons of all the soils except bG FSL. Such a deposition is a characteristic feature of podzols (13). This form of P was found to be posi-

TABLE 4

Relation of organic phosphorus to organic carbon and organic nitrogen

Soil Type	Horizon*	Carbon	Nitrogen	Phosphorus	C/N	C/P	N/P
		%	%	%			
bG FSL	A_{1a}	1.71	0.140	0.003	12.2	570	46.7
	A_{1b}	1.49	0.122	0.002	12.4	745	61.0
	B_1	0.97	0.098	0.009	9.7	108	10.9
	B_2	0.58	0.070	0.013	8.3	44	5.6
	B_3	0.36	0.035	0.013	9.0	27	2.5
DG FSL	A_{1a}	2.22	0.164	0.017	13.9	131	9.7
	A_{1b}	1.07	0.078	0.013	13.4	82	6.2
	B_1	0.62	0.067	0.023	8.9	27	3.1
	B_2	0.41	0.044	0.011	9.3	37	4.3
	B_3	0.24	0.028	0.008	8.0	30	4.0
G FSL/1	A	1.54	0.129	0.007	11.9	220	18.9
	B_1	0.97	0.077	0.009	12.1	108	8.9
	B_2	0.36	0.061	0.015	6.0	24	4.2
	B_3	0.23	0.054	0.010	4.3	23	5.4
G FSL/2	A	1.14	0.093	0.005	12.3	228	18.6
	B_1	0.87	0.081	0.005	10.9	174	16.2
	B_2	0.40	0.061	0.004	6.7	100	15.3
	B_3	0.26	0.051	0.006	5.2	43	8.5
gY FSL	A	0.84	0.080	0.008	10.5	105	10.0
	B_1	0.61	0.084	0.009	7.3	68	9.3
	B_2	0.82	0.083	0.015	9.6	54	5.5
	B_3	0.46	0.079	0.017	5.8	27	4.7
yG FSL	A	1.03	0.101	0.012	10.3	86	8.4
	B_1	0.39	0.060	0.011	6.5	36	5.5
	B_2	0.31	0.061	0.008	5.2	39	7.6
	B_3	0.27	0.049	0.008	5.4	34	6.1

* See table 1 for depths.

tively correlated with loss on acid treatment (tables 2 and 6), which represents primarily sesquioxides in pedalfer soils.

Fe-bound P

Fe-bound P was deposited in the B horizons of all the soils except bG FSL. This form of P showed a positive correlation with the free Fe_2O_3 content of the soils (tables 2 and 6).

Al-bound P

A surface enrichment with Al-bound P, which generally decreased with depth, was evident in all the soils except G FSL/1.

Adsorbed P

Mattson (12), Burd and Murphy (3), Stout (18), Black (2), Dean and Rubins (4), and others have shown that phosphate adsorption can be attributed pre-

TABLE 5

Distribution of different forms of potassium in soils and in clays

Soil Type	Horizon*	Total K_2O in Soil	Available K_2O in Soil		Adsorbed K_2O in Soil		Fixed K_2O in Soil		Fixed K_2O in Clay	Fixed K_2O in Non-colloid
		%	%	%†	%	%†	%	%†	%	%
bG FSL	A_{1a}	2.07	0.013	0.63	0.074	3.58	1.98	95.65	—	—
	A_{1b}	2.04	0.020	0.98	0.073	3.58	1.95	95.59	—	—
	B_1	1.96	0.008	0.41	0.044	2.25	1.91	97.45	—	—
	B_2	2.51	0.012	0.48	0.025	1.00	2.47	98.41	—	—
	B_3	3.19	0.018	0.56	—	—	—	—	—	—
DG FSL	A_{1a}	2.21	0.018	0.81	0.044	1.99	2.15	97.29	1.61	2.34
	A_{1b}	1.82	0.021	1.16	0.022	1.21	1.78	97.80	1.28	1.91
	B_1	2.95	0.015	0.54	0.013	0.44	2.92	98.98	0.98	4.38
	B_2	2.49	0.045	1.81	—	—	—	—	—	—
	B_3	2.49	0.073	2.93	0.074	2.97	2.34	93.98	1.19	3.36
G FSL/1	A	1.78	0.013	0.73	0.010	0.56	1.76	98.87	—	—
	B_1	2.35	0.013	0.55	0.048	2.04	2.29	97.45	—	—
	B_2	2.29	0.016	0.70	0.075	3.28	2.20	96.07	—	—
	B_3	2.27	0.034	1.50	—	—	—	—	—	—
G FSL/2	A	2.08	0.015	0.72	0.045	2.17	2.02	97.12	—	—
	B_1	1.92	0.016	0.83	0.065	3.39	1.84	95.83	—	—
	B_2	2.11	0.022	1.04	0.013	0.62	2.08	98.58	—	—
	B_3	3.66	0.027	0.74	—	—	—	—	—	—
gY FSL	A	2.12	0.011	0.52	0.014	0.66	2.10	99.06	0.97	2.41
	B_1	1.92	0.014	0.73	0.034	1.77	1.87	97.39	1.01	2.40
	B_2	2.62	0.050	1.91	—	—	—	—	—	—
	B_3	3.94	0.034	0.86	0.037	0.94	3.87	98.22	1.11	7.26
yG FSL	A	4.75	0.006	0.13	0.030	0.63	4.71	99.16	1.23	5.81
	B_1	3.93	0.016	0.41	0.028	0.71	3.89	98.93	1.28	4.91
	B_2	2.23	0.079	0.31	0.021	0.94	2.13	95.51	1.32	2.56
	B_3	5.12	0.014	0.27	—	—	—	—	—	—

* See table 1 for depths.
† Of total potassium.

dominantly to the kaolinitic aluminosilicates, the reaction being accompanied by a stoichiometric release of hydroxyl ions. The soils in the present investigation, with dominantly kaolinitic clay minerals (the SiO_2-R_2O_3 ratio of the clay minerals is around 2.0, as shown in table 6), also exhibited phosphate adsorption to a marked degree, the adsorbed P being as high as 27 per cent of the total P (table 3) in one case.

The adsorbed P indicated a distinct eluviation-illuviation process in the soils, resulting in an enrichment of the B horizons of all the soils except yG FSL and gY FSL. This process is evidently a podzolic one.

The adsorbed P showed a direct relationship with available P (table 2), indicating that the available P in the soils under investigation is probably a func-

TABLE 6

Distribution of loss on acid treatment, free iron oxide, total cation-exchange capacity, and silica-sesquioxide ratio in the profiles

Soil Type	Horizon	Loss on Acid Treatment	Free Iron Oxide	Total Cation-Exchange Capacity of Clay	$\frac{SiO_2{}^*}{Al_2O_3 + Fe_2O_3\dagger}$
		%	%	*me./100 g.*	
bG FSL	A_{1a}	0.72	2.52	43.6	2.02
	A_{1b}	1.08	2.74	53.0	1.90
	B_1	2.01	3.58	48.4	1.10
	B_2	1.85	4.00	46.1	1.93
	B_3	0.20	4.06	—	—
DG FSL	A_{1a}	0.02	1.72	42.6	2.07
	A_{1b}	0.54	2.03	50.8	1.84
	B_1	1.46	3.13	43.0	2.23
	B_2	1.15	3.51	—	—
	B_3	1.96	3.37	41.9	1.92
G FSL/1	A	0.90	1.59	59.0	2.12
	B_1	1.57	2.03	70.4	2.00
	B_2	1.67	3.83	48.8	1.96
	B_3	0.80	3.84	—	—
G FSL/2	A	0.44	2.08	52.5	2.06
	B_1	1.93	2.22	60.9	2.16
	B_2	1.72	3.40	50.1	1.96
	B_3	1.72	3.51	—	—
gY FSL	A	0.46	1.91	49.1	1.90
	B_1	0.75	2.44	45.2	1.98
	B_2	0.63	1.92	—	—
	B_3	2.85	2.88	47.5	2.66
yG FSL	A	0.33	1.76	58.2	1.92
	B_1	0.90	2.17	52.9	2.01
	B_2	0.69	2.13	41.7	2.01
	B_3	0.68	3.25	—	—

* See table 1 for depths.
† Gram-molar ratios on ignited clay.

tion of adsorbed P. This finding is in agreement with that of Birch (1), who observed that adsorbed P is efficiently available to plants.

DISTRIBUTION OF DIFFERENT FORMS OF POTASSIUM

Results of the analyses of available, adsorbed, and fixed forms of potassium (mainly in potash-bearing soil and clay minerals) are given in table 5.

Available K_2O

Available K_2O accumulated in the subsurface horizons of the profiles of all soils except bG FSL. This form of K_2O represents a very small fraction of the total K_2O reserve of the soils.

Adsorbed K_2O

Adsorbed K_2O showed a subsurface accumulation in G FSL/1, G FSL/2, and gY FSL. Again, all the soils except bG FSL showed an enrichment of adsorbed K_2O, considered as percentage of total K_2O, in the B horizons. Adsorbed K_2O was directly, though very slightly, correlated with available K_2O (table 5).

Fixed K_2O in colloidal and noncolloidal fractions

Fixed K_2O comprised about 95 per cent of the total K_2O of the soils. This fixed form in soil, however, may belong to both the colloidal and noncolloidal fractions, and the fixed K_2O content of both these fractions has been individually considered with a view to assessing the presence of any potassic mineral in the clay and also in the coarser fractions of the soils.

Table 5 shows that the noncolloidal fractions of the soils contain a considerable amount of potassic minerals—micaceous or glauconitic—a feature suggesting a recent marine origin of the soil materials (16).

The presence of fixed K_2O in the clay fractions of the soils indicates the probable presence of illite in the clay minerals. In light of the findings of Grim *et al.* (6) and Karim (9), the low content of this form of K_2O suggests that illite comprises only a minor fraction (not more than 15–25 per cent) of the clay minerals. This implies that the relevant clay minerals are dominantly kaolinitic.

The total cation-exchange capacity of the clay, calculated (table 6) in light of Karim's (9) findings, was too high (40 to 70 me./100 g.) for the dominantly kaolinitic clays of the soils. This indicates that probably some other fraction of the soil, namely, silt, which in recent years, has been reported also to exhibit exchange phenomena to some degree (9, 10), has contributed toward the total cation-exchange capacity.

SUMMARY

A study of the distribution of different forms of nitrogen, phosphorus, and potassium in the profile and its bearing on the pedogenic characteristics of some gray-brown podzolic soils of East Pakistan led to the following observations:

Organic nitrogen gradually decreased down the profiles. It constituted the bulk of total nitrogen. The ammonia and nitrate nitrogen content of the soils was very low. An eluviation-illuviation of different forms of phosphorus; namely, inorganic, organic, R_2O_3-bound, Fe-bound, and adsorbed P has taken place in the profiles.

The rate of breakdown and disappearance of organic P down the profiles was much less than that of organic C. The average C/P and N/P ratios of the soils were 122 and 11.8 respectively.

Adsorbed P showed a positive correlation with available P.

Adsorbed K_2O also showed a direct though slight relation to available K_2O.

Fixed K_2O, which constituted the bulk of total K_2O, may be related to the potassium-bearing minerals in colloidal and noncolloidal fractions. The fixed K_2O in the clay fraction of the soils suggests the presence of illite in the amount of 15–25 per cent, thereby implying a predominantly kaolinitic nature of the clays (confirmed by the low SiO_2–R_2O_3 ratio).

The high value for the cation exchange capacity of the clays of the soils was sought to be accounted for by accepting the view that silt too contributed towards cation exchange reactions.

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AGROBIOLOGIC PERCENTAGE METHOD OF EVALUATING FERTILIZER TESTS: III. QUANTITATIVE AGROBIOLOGIC ANALYSIS OF A FACTORIAL EXPERIMENT

O. W. WILLCOX

Consulting Agrobiologist[1]

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In previous papers (6, 7) a basis was laid for the agrobiologic percentage method of evaluating fertilizer tests as a substitute for and improvement on current statistical methods involving analysis of variance according to Fisher, Yates, Snedecor, Cox, and other authors of statistical methods manuals for agricultural workers. This percentage method is derived from the Mitscherlich yield equation, accepted by quantitative agrobiologists as the sole authentic mathematical expression for the law of diminishing increments of yield in agriculture, the plant-biological phase of the general economic law of diminishing returns.

The first step in applying this percentage method to evaluation of a field or pot test is to identify that Mitscherlich-Baule curve which best fits the experimentally determined yields as functions of incremental applications of fertilizer *measured in baules*. Identification of the appropriate curve is facilitated by use of the standard agrobiologic yield diagram as previously explained (2, 3). When the soil is of uniform composition all the experimental yields will fall on or close to a single standard curve, with the range of deviation proportionate to the care exerted by the operator in his experiment. The operator will then note the deviations of his experimentally determined yield points from this curve. For each point he will calculate the difference between what he has found and what the curve theoretically requires for a perfect fit, expressing the difference as a percentage of what he has found. From the sum of these percentage deviations the average deviation is first determined and then subtracted from 100 to give the percentage of probability that the same yields could be reproduced if the experiment were repeated under the same conditions. The probability figure so obtained is the agrobiologic substitute for what contemporary experimental statisticians designate as "significance."

The main reason that warrants this substitution is that (*a*) significance arrived at by analysis of variance is purely abstract, undifferentiate, and void of direct connection with the realities of plant nutrition now known to subsist in the quantitative relations between plants and their nutrients; and (*b*) it is incapable of taking quantitative account of these relations. In other words, analysis of variance, proceeding from the abstract general theory of probability (Gauss) which does not contemplate the existence of a foreordained structure or orderly sequence of change within systems into which variance may be thrust by extraneous influences, is out of place when applied to the process of plant nutrition, for plant nutrition is normally under the exclusive control of the very

[1] 197 Union St., Ridgewood, N. J.

definite, specific natural law of diminishing increments of yield (Mitscherlich-Baule-Willcox). In accord with the tenets of this specific natural law, therefore, the results of a fertilizer test must be evaluated by a direct, individual comparison of each experimentally determined yield with the corresponding theoretical yield set up by the law for that specific case.

When the plant nutrient content of the soil is uniformly distributed over the test area, the standard yield diagram will give users little difficulty in diagnosing the amount of fertilizer needed to produce a maximum yield. In numerous cases, however, the soil or parts thereof may be of heterogenous composition, or the soil may be affected by certain influences that impose a systematic disturbance of the normal nutrition of the experimental crops. How to handle the situations thus created can be ascertained after some experience with the standard agrobiologic yield diagram. In previous papers (3, 4) the principal sources of systematic disturbance have been defined and named, and a normal situation and cases involving "scattering" and "near-end depression" described (7). The present paper deals with a case of "far-end depression," which experience has shown to be the most common and most damaging of the aberrant situations the working quantitative agrobiologist[2] is likely to encounter.

EXPERIMENTAL DATA

The field experiment selected for this discussion [taken from a report by Roussel (1) on a 4–4–3 factorial test with sugar beets in Belgium] involved three variants: variety, rate of nitrogen fertilizer use, and date of harvest. Forty-eight objects, each in four replications totaled 192 individual plots. The four varieties (V_1, V_2, V_3, V_4) included one strain of normal yielding ability; one, high-yielding; and two, extra-high yielding. The increments of added nitrogen (N) fertilizer were: 70, 120, 170, and 220 kg./hectare, amounting to 0.28, 0.48, 0.68, and 0.88 baules/hectare. The dates of harvest were September 28, November 2, and November 30. The writer plotted Roussel's data (fig. 1) on four replicas of that sector of the standard agrobiologic yield diagram which would accommodate all 12 curves; thus the yields of each variety corresponding to its three dates of harvest (H_1, H_2, H_3) are shown separately. This avoids considerable overlapping of curves, which would impair clarity of presentation. The scaling of the horizontal axis is in baules (1 baule of N = 250 kg./hectare, or 223 lb/acre). Relative yields of factory beets, reported as thousands of kilograms per hectare, and obtained by dividing Roussel's yield figures by the factor 5000, were scaled on the vertical axis.

[2] The term "quantitative agrobiology" is intended to designate that branch of plant science which deals with exact quantitative relations between plants and factors of their growth, in contrast to "ecology," which is concerned with general or qualitative relations of plants to their environments. Because of its emphasis on quantitative measurement, quantitative agrobiology may be regarded as the stoichiometric armamentarium of plant physiology, which in its ordinary phase is limited to discussion of qualitative experiments in plant metabolism.

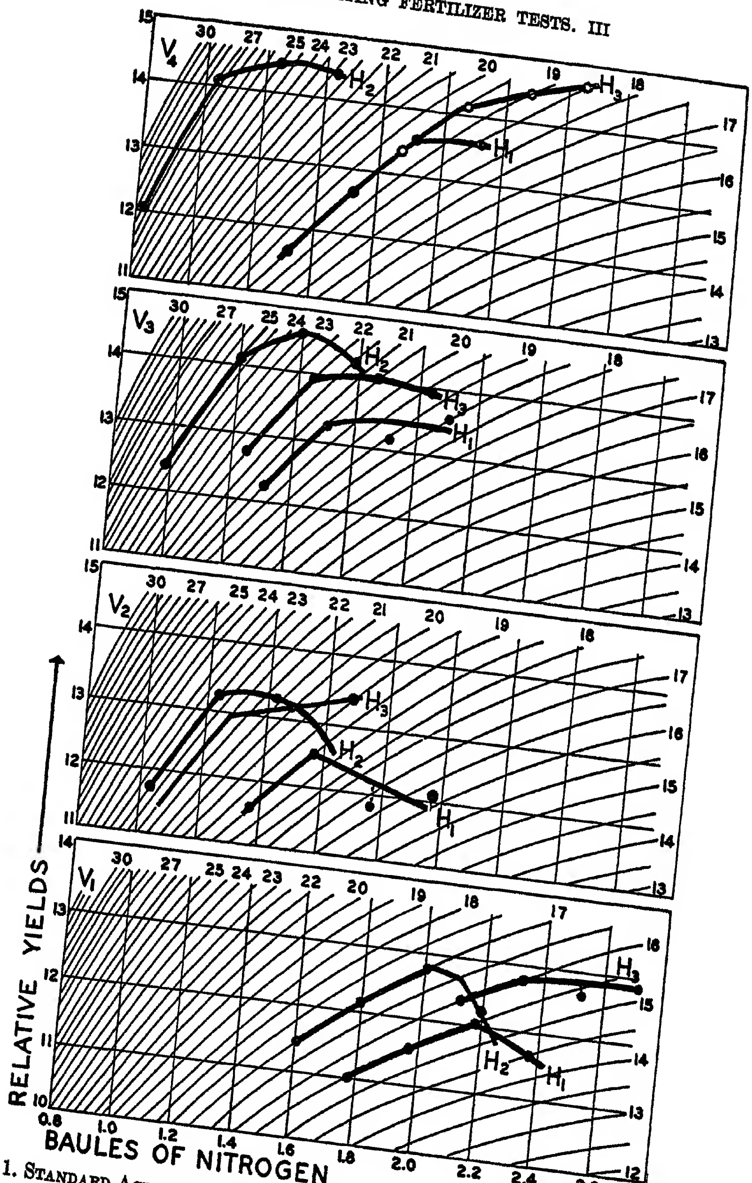

FIG. 1. STANDARD AGROBIOLOGIC YIELD DIAGRAM OF ROUSSEL'S 4-4-3 FACTORIAL TEST ON VARIETIES, RATE OF NITROGEN FERTILIZER USE, AND DATES OF HARVEST

Numerals in the margins represent values of A.

CHARACTERISTICS OF THE YIELD CURVES

A great advantage of plotting yields on the standard agrobiologic yield diagram, with growth factors measured in baules, is that results are shown in a perspective that would be difficult to visualize from a numerical tabulation of the experimental data, even if these data were conventionally plotted with the horizontal axis scaled for common units of weight.

An experienced quantitative agrobiologist will see at once that the diagrams in figure 1 show a case of far-end yield depression imposed on two soil-fertility gradients. It is characteristic of curves showing far-end depression that the yield points corresponding to the smaller additions of a growth factor (here N) fall normally on one standard curve, but they break away from the normal curve at a more or less sharp angle when the quantity of added N has been increased to a certain degree. With continued additions of N to the soil, the upper limb of the curve deflects to the right and may turn downward, causing the whole curve to resemble an inverted fishhook. Curves representing the middle date of harvest (H_2) especially suggest such a comparison. It is noteworthy that the H_2 curves lie farthest to the left on all four diagrams. The significance of this fact is discussed later.

Though far-end depression may result from an excess of any growth factor, it is much more common in fertilizer operations with nitrogen. This may be ascribed to the fact that it takes more nitrogen to constitute 1 baule of this factor (250 kg./hectare) than, for example, a baule of P_2O_5 (50 kg./hectare). Consequently, if the bauleic concentration of nitrogen is excessive in comparison with other factors, the plants will be more or less subjected to plasmolysis and their yield proportionally reduced, especially in dry seasons when concentration of soluble nitrogen compounds in soil moisture may become decidedly harmful.

The diagrams also show that the points where plasmolysis and loss of potential yield begin are different in different sections of this experiment. For example, the curve of V_4H_2 deflects when the total N content of the soil (original plus added N) is about 1.20 baules, V_3H_2 deflects at 1.39, V_2H_2 at 1.43, and V_1H_2 at 1.96 baules. This situation might be misinterpreted to mean that V_4 is the least and V_1 the most resistant to large additions of nitrogen.

The prevalence of far-end yield depression is a serious handicap in efforts to increase the yielding capacity of the soil. A later section indicates the extent to which this phenomenon has interfered with sugar beet production on this Belgian soil.

MAXIMUM POSSIBLE YIELDS

What primarily interests the agronomist using the standard agrobiologic yield diagram is the quantity of a plant nutrient (b) contained in the untreated soil, and the maximum yield (A) obtainable by extended application of the nutrient in question, so that intermediate values of y and x may be calculated by the Mitscherlich-Baule equation:

$$\log (A - y) = \log A - 0.301 (x + b)$$

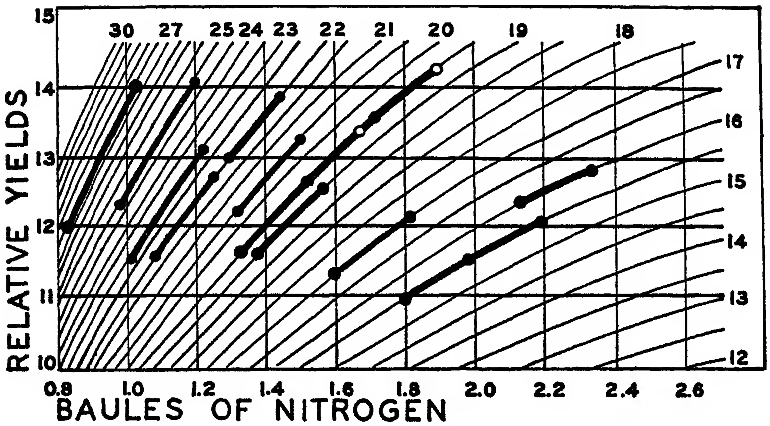

FIG. 2. NORMAL LOWER LIMBS OF CURVES DRAWN FROM ROUSSEL'S DATA
Note the homologous orientation of these limbs toward the common point of origin.

When the data of a field test are plotted on the standard yield diagram, the value of A will be indicated by that normal curve on which most of the experimental yield points make a reasonably close fit. In the present case the normal curves of V_1H_2, V_1H_1, and V_4H_1 are each defined by three experimental points, which give the values of A as 17.0, 15.5, and 19.5, respectively. The fourth points of these three curves are out of line, because of the incidence of far-end yield depression. In each of the nine other curves only the two lower points fall on normal curves.

A geometrician might raise an objection to what looks like the use of only two points to define a normal yield curve, when at least three points are necessary. But the Mitscherlich-Baule curves always have one point in common on which they all converge—the point of origin, where $y = 0$ and $x = 0$. Thus, in fact, three points are used. The maximum values of A are shown in the third column of table 1. In confirmation of the propriety of accepting the first three points as determinative of the normal limbs of these curves, it may be pointed out (as in figure 2) that they are all homologous, that is, they all fit closely on standard curves of very different slopes. Obviously, all are obeying the same natural law.

PRECISION OF THE PERCENTAGES

How well do Roussel's experimental yields fit on standard curves? On the normal lower limbs, the range of deviations from theory and the percentage relation of these deviations to the theoretically calculated values are shown in the sixth and seventh columns of table 1. Three of the 27 objects (yield points) classified as normal show deviations above 1 per cent (maximum deviation 3.41 per cent); in the other 24 normal objects the deviations are below 1 per cent and the average deviation is 0.492 ± 0.103, which indicates an agrobiologic probability of about 99 per cent and may be regarded as the agrobiologic equivalent of what a professional statistician would accept as significance at

TABLE 1

Characteristics of normal limbs of curves drawn from Roussel's data

Object	Baules of N (x)	Units of Yield			Differences	
		Maximum A	Calculated y	Obtained y	Units	% of obtained y
$V_1H_1N_1$	1.76	15.5	10.92	11.00	0.08	0.73
N_2	1.96	15.5	11.60	11.49	0.11	0.96
N_3	2.16	15.5	12.03	11.95	0.08	0.67
$V_1H_2N_1$	1.60	17.0	11.39	11.33	0.06	0.53
N_2	1.80	17.0	12.11	12.15	0.04	0.33
N_3	2.00	17.0	12.75	12.75	0.00	0.00
$V_1H_3N_1$	1.96	16.0	11.88	12.30	0.42	3.41
N_2	2.16	16.0	12.42	12.75	0.33	2.60
$V_2H_1N_1$	1.36	19.0	11.62	11.60	0.02	0.17
N_2	1.56	19.0	12.54	12.53	0.01	0.08
$V_2H_2N_1$	1.08	23.0	11.59	11.55	0.04	0.35
N_2	1.28	23.0	12.97	12.95	0.02	0.02
$V_2H_3N_1$	1.06	22.0	11.61	11.75	0.14	1.19
N_2	1.26	22.0	13.30	13.30	0.00	0.00
$V_3H_1N_1$	1.31	20.5	12.22	12.30	0.08	0.65
N_2	1.51	20.5	13.30	13.30	0.00	0.00
$V_3H_2N_1$	0.99	25.0	12.41	12.35	0.06	0.49
N_2	1.19	25.0	14.04	14.05	0.01	0.07
$V_3H_3N_1$	1.24	22.0	12.71	12.70	0.01	0.08
N_2	1.44	22.0	13.91	13.85	0.06	0.43
$V_4H_1N_1$	1.45	19.5	11.69	11.65	0.04	0.34
N_2	1.52	19.5	12.70	12.69	0.01	0.08
N_3	1.72	19.5	13.58	13.55	0.03	0.22
$V_4H_2N_1$	0.82	27.5	11.95	12.00	0.05	0.42
N_2	1.02	27.5	13.95	14.05	0.10	0.71
$V_4H_3N_1$	1.66	19.5	13.35	13.32	0.03	0.23
N_2	1.86	19.5	14.14	14.13	0.01	0.07

Sum of deviations: 14.83. Mean deviation: 0.492 ± 0.103. Probability about 99%.

the 1 per cent level. The probability that the normal limbs of these curves could all be reproduced if the work were repeated under the same conditions is thus a 99:1 chance. The settings of the points on the depressed upper limbs are irregular and abnormal, because of the varying intensity of the cause that produced depression; no two of the depressed yield points can be fitted on any regular curve that passes through the common origin.

RELATIVE MAGNITUDES OF THE YIELD DEPRESSIONS

A Mitscherlich-Baule curve rises from its origin and traces a logarithmic course until it virtually merges with a horizontal line marking a limit of yield, which cannot be increased by a further increase in the soil's content of plant nutrients. The maximum yield is attained when no further increase results from a further application of fertilizer. If, however, a yield depression has intervened, the actual maximum yield will be less than the theoretical maximum.

For example, in V_4H_2, for which the theoretical maximum yield (A) was 27.5 relative units, the normal rate of increase was interrupted at ordinate 1.22 by the onset of depression, but after application of the second increment of nitrogen fertilizer, there was a further slight increase from 12 to 14.5 units of yield, then the curve began to turn down. The difference between the theoretical and the actual maximum was thus 13.0 units, or 47 per cent of the possible maximum. Again, in V_2H_2 the theoretical maximum A was 23.00; depression began at ordinate 1.32, and under the influence of continued applications of nitrogen fertilizer the final yield was only 12.95 units. The theoretical shortage here was 44 per cent. The same story is repeated for V_1H_2 and V_1H_1.

In the eight other tests of date of harvest the degree of depression was obviously less pronounced. The hooked form is absent from all H_3 curves, which take a position between H_2 and H_1 and continue to rise, though at a reduced rate. It is also absent from V_4H_1 and V_3H_1, but tends to reappear in V_2H_1 and V_1H_1.

ANOMALIES

Apparent anomalies, which may be observed from a study of figure 1 as a whole, are cleared up by a close examination of the 12 curves in their four divisions.

The wish for soil of uniform composition on which to make a field test is seldom realized, especially when the number of experimental plots is large (here 192). An extensive test area is likely to mean great soil heterogeneity with variance in one or more essential factors. Consider first the normal H_2 curves. The standard yield diagram indicates that the average initial content of nitrogen (b) in the soil of the plots which produced curve V_4H_2 was 0.82, V_3H_2 0.99, V_2H_2 1.08, and V_1H_1 1.76 baules. This obviously means a marked upward gradient of original soil nitrogen content from the left to the right side of the diagram, a fact confirmed by the relative positions of each of the eight other curves. The over-all fertilities of these subdivisions of the test area were not increased by the successive applications of added nitrogen, but actually decreased. Thus, for example, the normal limb of curve V_4H_2 at the upper left approached the limit $A = 27$, V_3H_2 the limit $A = 25$, V_2H_2 the limit 23, and V_1H_2 the limit 17. Normal yields likewise decreased from left to right in the same descending order of magnitude in all other divisions of date of harvest tests.

This apparent anomaly seems to contradict the general experience that when crops are planted on a supposedly uniform soil deficient in a certain plant nutrient, an increase in the quantity of that nutrient results in an increase of yield. Here, however, the more the quantity of nitrogen in the soil was increased, the smaller were the normal yields of the crops. This deviation from the ordinary rule of "more fertilizer, more yield" in this factorial test automatically proves that in spite of the increase of nitrogen fertilizer from left to right on the diagram, the divisions of the area allotted to the four varieties were affected by a soil-fertility gradient which also descended from left to right.

Though the diagram rigorously sets the normal value of A that should be

obtained in absence of depression, the diagram is apparently contradictory in the depressed upper limbs of some of the curves (*see* V_4, V_2, V_1). In these cases the highest yield obtained in H_3 exceeds the highest yields in H_2; that is, the rule of "more fertilizer more yield" is asserting itself. The explanation is that the depressed limbs of these H_3 curves have the more favorable position in respect to the varying soil fertility and are still rising, whereas the depressed H_2 curves in the less favorable positions are hooked.

PRESENCE OF SECOND FERTILITY GRADIENT

These yield diagrams also demonstrate the presence of another fertility gradient, which is ascending in the opposite direction—from right to left. This gradient is revealed through consideration of postulates inherent in the agrobiologic law of yield as formulated by Mitscherlich. Growth and yield of all kinds of plants depend on the same limited group of factors: light, temperature, water; the same group of chemical plant nutrients, including N, P, K, Ca, and other alkaline elements; S, Fe, and others of the heavy metal group, together with a soil in a physical condition appropriate to establishment of aerobic conditions in the roots zone.

These various factors of plant growth are coequal in their potencies for increasing crop yields, and the *baule*, or the quantity necessary and sufficient to account for 50 per cent of a maximum possible yield (A) may be defined for each factor. Not only are these factors coequal in nutrition value, but are equally indispensable. Each must be present and in operation; if any one is absent there will be no yield; and, for a normal increase in yield, they must all be present in the same numbers of baules. If one is present in a smaller bauleic concentration than the others, the normal yield will be reduced in proportion to the shortage of the deficient factor. For example, if the bauleic concentration of the deficient factor is enough for only a 64.64 per cent yield (1.5 baules) while the other factors are present in amounts for a 93.75 per cent yield (4 compound baules), the actual yield will be only $0.6464 \times 0.9375 = 0.6060$, or 60.6 per cent of the possible maximum. But, as previously mentioned and as emphasized in figure 1, differences in bauleic concentrations must not be too great; if the bauleic concentration of one chemical factor is predominant, the plants may be more or less plasmolyzed, and the yields will be depressed below the calculated values.

Applying these considerations to the case in hand, we see a plausible reason for the apparent reversal of the rule of "more fertilizer, more yield." As we go from left to right on the diagrams, the normal responses to nitrogen become less and less while the yields decrease. This apparent decrease in the efficacy of the nitrogen factor must in reality be due to the existence, in this direction, of a progressive decrease in the bauleic concentration of some other factor; the record does not enable us to identify the factor, but its influence is clearly discernible.

While the deficit of this unidentified factor, which we will call Z, grows from left to right, the deficit of nitrogen in the untreated soil is growing from right to left. We should expect, then, that at the left Z would be more or less predominant

over N, and at the right N would tend to dominate over Z. Yield depression should thus be expected to be accentuated on the left, less accentuated in the middle (where the two variables are more or less balanced), and more accentuated again at the right, which is mostly what we do see on the diagrams. The depression effect is strong on the H_2 curves, all of which represent yields from soils with the least amounts of original N and presumably the largest amounts of Z; and these curves are those most marked by the hooked form. Farther to the right the hooked form disappears from the H_3 curves; here the depressed limbs are either flat or rising at a rate lower than normal. Still farther to the right the hooked form tends to reappear in the H_1 curves, an indication that N is becoming predominant.

In this connection it will be instructive to observe curves V_4H_1 and V_4H_3. The normal limbs both indicate 19.5 as the common value of A. But the division on which V_4H_1 was planted had only 1.45 baules of N while V_4H_3 had 1.64. This means that V_4H_1, beginning farther to the left, had less N and more Z, while V_4H_3, beginning farther to the right, had more N and less Z. These two combinations were so agrobiologically balanced that each provided the requirement for a curve defining the same maximum yield. A comparable situation affects V_3H_3 and V_2H_3, where the normal limbs both indicate $A = 22.0$.

The diagrams show another anomaly that helps to confirm the existence of two fertility gradients on this test field. Yields from intermediate harvests of factory beets from the H_2 division (represented by the normal H_2 curves) were greater than those from the H_3 division harvested later. This again seems to contradict universal experience. The sugar beet, a biennial plant, is grown for sugar only in its first year, and beet growers strive to lengthen the growing season by planting early and harvesting on the last possible date before freezing weather. Normally, beets harvested on November 30 will yield distinctly more than those harvested on November 2. Here, however, we find that the earlier harvest was more abundant than the later.

The agrobiologic explanation for this reversal of the usual order is that, in relation to the progressive change in the proportions of Z and N due to the two oppositely oriented fertility gradients, the Z-N combinations on the H_2 division happened to be powerful enough in comparison with the N-Z combination on the H_3 division to more than compensate for the shorter growing season. At this distance we will not speculate on the probable nature of Z, beyond suggesting that it might have been soil moisture (Roussel notes that the season in which the test was made, April to August, was unusually dry) or perhaps a combination of factors.

Though Roussel reported the percentage sugar content of the beets and the yields of sugar and foliage per hectare, we have concerned ourselves here only with the yields of factory beets, since other quantitative aspects of the test are all qualitatively affected in common by the incidence of depression.

DISCUSSION

Roussel mentioned the Mitscherlich equation casually but made no attempt to apply it to his data. He made a conventional analysis of variance and deduced

TABLE 2

Roussel's ratios of variances for yields of sugar beets

Origin of Variation	F Values		
	Fisher	Snedecor's table	
		$P = 0.05$	$P = 0.01$
Dates of harvest, H	32.00	3.06	4.75
Varieties, V	60.06	2.67	3.91
Nitrogen, N	42.62	2.67	3.91
Interactions, HV	1.50	2.16	2.92
HN	1.76	2.16	2.92
VN	1.71	1.94	2.53
HVN	1.63	1.97	2.65

values of F corresponding to the principal criteria of the sugar beet; for each of the factors H, V, and N; for the first order interactions HV, HN, and VN; and for interaction of the second order, HVN. His figures for ratios of variances for yields of factory beets are shown in table 2. From these statistics it is deduced that the effect of the principal factors is definitely positive, even at the 0.01 point, which is no more than a statement of the good probability that the general results of the work are reproducible. This is as far as analysis of variance ever takes an agricultural worker who makes a vegetation test with fertilizer. As a result, he is left uninformed on matters of vital concern. Any system of soil testing as a basis for the use of a fertilizer is incomplete if it does not give an accurate measure of both the amount of that material already present in the soil and of the yield obtainable by its extended use. In the present case the standard agrobiologic yield diagram does give the required answers within accurately known limits (99:1).

Roussel's experiment is a classic demonstration of how the shortcomings of analysis of variance as a source of agronomic information multiply as the number of variables is increased. When for his 48 objects and their replications he had to use an extensive area, he incurred a risk of soil heterogeneity, which the diagram shows to have been both wide and varied. His variance analysis gives no hint of the existence of two oppositely oriented fertility gradients, or of the resulting anomalies that affect comparison of fertilizer effects and comparison of dates of harvest; yet these anomalies readily come to light on the standard yield diagram. Also, because of the demonstrated soil variability, the variance analysis does not give a sharp definition of the relative yielding abilities of the four varieties. The experimental data do show that the descending order of yield is V_4-V_3-V_2-V_1, which was already known from commercial practice. The diagram shows the A value for V_4H_2 as 27.5 and for V_1H_2 as 17.0, a spread of 56.5 per cent, which is not warranted by experience with these varieties. But suppose that the positions of curve V_4H_2 at the top of figure 1, where the complex Z/N is favorable, and of curve V_1H_2 at the bottom, where N/Z is less favorable, were interchanged. The difference between the A values would then probably be considerably reduced, if not reversed.

AGROBIOLOGIC DESIGN FOR A FIELD TEST WITH GROWTH FACTORS

The only values definitely established in this factorial test are for the quantities of nitrogen in the soils of the 12 divisions of the field after addition of the first applications of fertilizer. These initial contents of N ranged from 0.82 to 2.08 baules (average 1.438 ± 0.278 baules/hectare or 319.9 ± 69.5 lb./acre). That is, with the first application added to the existing residual N, the field as a whole had enough N to produce 63 per cent of the maximum yield (A) attainable from extended use of N by any of the four varieties. But, as we have seen, the anomalies created by soil variability affecting the four areas of the field have left the real values of A and the effects of varied harvest dates in considerable doubt. A field of uniform nutrient composition would furnish the condition necessary to establish the real values of these parameters, but such a field of the requisite area is seldom found. The only other recourse would be an experiment so designed as to minimize to the fullest possible extent the effect of soil variability.

According to this writer's observations, the appropriate design is found in the old-fashioned strip test, which recently has been given a new look. The revitalized strip test consists in laying out a long, narrow block that is longitudinally divided into three strips of equal widths. In a nitrogen test, for example, the two outer strips are left unfertilized, the inner strip receives an application of N, which is *measured in baules*, and the whole block is planted with the test crop. At harvest the yields of the three strips are weighed separately; the yields of the two outer strips are averaged and this average is subtracted from the yield of the treated strip. The difference obtained is then used to calculate the original N content of the soil and the maximum yield (A) that could be attained by extended use of N on that field. Details of this calculation, which is facilitated by use of two simple diagrams, were given in a previous paper (5).[8]

Variations of soil fertility do not usually occur abruptly. The variance is gradual, as on Roussel's field where we found two gradients developing in opposite directions. If on such a field we consider three contiguous narrow plots a, b, c, the gradient proceeding in either direction will be more (or less) manifest at a, less (or more) at b, and still less (or more) at c. Since the distance between the center lines of the strips is short, the original fertility of b is very likely to be a close average of the original fertilities of a and c; and since these two strips constitute two thirds of the whole area of the untreated block, the average of their original fertilities must be very close to the average original fertility of the whole block. Their average yield, therefore, can be taken as a reliable base for assessing the increase of yield produced by the fertilizer applied to b.

In practice, the strips need not be wide. With beet rows 18 inches apart, a width of 6 feet will accommodate four rows, two of which may be treated as guard rows. Other crops may require wider spacings. In any case, since the fertility drop or increase over a short distance will be inconsiderable, soil variance will be reduced to the fullest practicable extent. No limit need be placed on the

[8] A limited number of reprints of this paper are available.

length of the block. If a stretch of 1000 to more than 1200 feet is available, it may be divided into sections of 100 or 150 feet and the yields of these sections evaluated separately by the percentage method. This elongated block will then give a fertility profile across the entire width or length of the field, and may show up variances that would not be indicated by a more compact block of equal area.

For a variety test a number of parallel narrow strips may be laid out and denoted as 1, X_1, 2, X_2, 3, X_3, 4, etc. Strips 1, 2, 3, 4 will be planted with a variety of known productivity and the X strips with the varieties to be tested. At harvest, the yield of an X strip is compared percentagewise with the average yield of its two flanking strips. Date of harvest tests may be handled in the same way.

CONCLUSION

In this and previous papers it was shown that a variance analysis of the results of field tests with fertilizers does not supply the operator with any real information on the situation on his test field. Such tests are made to determine whether use of fertilizers would improve the yields of useful plants and by how much. The most a statistician who uses this method can offer is an abstract figure, called "least significant difference," that is supposed to measure the reliability of experimentally found differences. But in specific cases (2) these least differences may be grossly misleading.

This defect of the variance method arises from the fact that the method, being abstract, has no concrete base in the specific natures of either plants or fertilizers, which are under the exclusive control of a general law of the vegetable kingdom: the law of diminishing increments of yield, which is known to apply to every species of rooted and green-leaved plant that has yet come under quantitative study. No method of evaluating fertilizer tests has any color of authenticity if it does not approach from the standpoint of this general, peremptory natural law of the plant world. When this approach is made (as described in the present paper) the operator is informed of: (*a*) the amount of the test fertilizer present in the untreated soil; (*b*), the degree of variability (if any) in the distribution of this original fertility; (*c*), the maximum yields attainable by extended application of the test fertilizer on the various divisions of the test area; and (*d*), the presence or absence of circumstances that may block attainment of the possible maximum yields. None of this vital information is given by a conventional analysis of variance.

Since the variance analyst's major premise has no specific relation to the quantitative agrobiologic realities of plant life, which are fixed by the law of diminishing increments, his methodology in this field lacks realism. Agrobiologists discard Latin squares, randomized plots, t tests, and F values to find satisfaction in the modern strip test, the one obvious method of reducing soil variability to the lowest attainable minimum.

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Activities of FAO Under The Expanded Assistance Program 1953/54. By Food and Agricultural Organization of the United Nations. Columbia University Press, New York, 1955. Pp. 88. Price $0.50.

The Technical Assistance Program had $5,536,000 at its disposal for 1954. This report shows how this money was spent in the many countries in which the program is operating. The number of persons employed in the program varies between 1 and 20 per country. United Kingdom, The Netherlands, and the United States, in that order, supplied the largest number of experts.

Advances in Agronomy. Volume 8. Edited by A. G. NORMAN. Academic Press, Inc., New York, 1955. Pp. 431. Price $8.80.

Prepared under the auspices of the American Society of Agronomy, this latest volume contains papers on soil aggregation (including soil conditioners), Swedish crop production, microbes in relation to plant nutrition, sugar beet improvement, green manuring, plant introduction, soil nitrogen balances, weed control in southern U.S.A., mineralization of organic nitrogen in soil, and the place of microbiology in soil science. The quality of the several papers varies greatly, some of them being of only passing interest, and others having permanent value. Among the latter, the 100-page paper on nitrogen mineralization by G. W. Harmsen and D. A. Van Schreven, both of The Netherlands, merits special mention. This is a careful, unbiased review of the literature, devoid of extraneous and opinionated material. It merits very careful reading by those who are interested in this subject. A bibliography of some 600 items is appended to this paper.

Atomic Energy Research at Harwell. By K. E. B. JAY. Philosophical Library, New York, 1955. Pp. 143, plates 19, figs. 9. Price $4.75.

This report is an extension of one published in 1952 under the title "Harwell—The British Atomic Energy Research Establishment, 1946–1951." It starts with a glossary of technical terms and then tells of some of the advancements that have been made in the production, reactor, and isotope programs. This is followed by discussions of electronic instruments, special techniques, and engineering. In the discussion of the use of radioactive tracer methods, notably with phosphorus and iodine, an interesting observation is made on the use of the latter element in measuring the volume of blood in a human patient and in locating cerebral tumors. The second half of the book, written in more technical terms, deals with specific items of research in physics, chemistry, engineering, and metallurgy. Bibliographies are attached to these chapters. The book contains come interesting graphs and plates. The director of the staff is John D. Cockcroft.

Aux Sources de la Pédologie, By H. MARGULIS. L'Ecole Nationale Supérieure Agronomique de Toulouse, France, 1954. Pp. 85, charts, 3.

The author is of the opinion that Glinka's interpretation of Russian pedological

concepts, on which most of the workers in this field of study have depended, gave greater emphasis to climate than the originators of the concepts had originally intended. He reviews the Russian concepts in considerable detail, presenting two charts on soil classification, one that of Doukoutchaiev and the other that of Sibertzev, his student. Also shown is a schematic map of the chernozem of European Russia, based on the percentage of humus in the soil. Photographs and short biographies of both men are included. This is a highly interesting presentation of the subject and merits careful reading by those concerned.

Biochemical Preparations. Edited by W. W. WESTERFELD. John Wiley and Sons, Inc., New York, 1955. Pp. 108. Price $3.75.

This is volume 4 of the series. It covers the principles, starting materials, procedures, properties, purity, and methods of preparation of 21 biochemical substances. These include alcohol dehydrogenase and inorganic pyrophosphatase. References are appended for each material. This is a valuable aid to those interested in such preparations. Volume 5 of the series is in preparation.

Climates in Miniature. By T. BEDFORD FRANKLIN. Philosophical Library, New York, 1955. Pp. 137, plates 8, figs. 10. Price $3.75.

The subtitle of this book is "A study of microclimate and environment." Microclimate is defined in relation to hibernation, cranberry bogs, soils, earth and air temperatures, rain, frost, humidity, dew, wind and shelter, light and shade, cloches, and frames and in relation to the farm and home. The book is highly interesting and instructive. Among the many subjects dealt with is that of dew ponds and stone pyramids for collecting water. It is quite apparent from the book that there are many possibilities for useful research in exploring microclimate.

Contributions to Plant Anatomy. By IRVING W. BAILEY. The Chronica Botanica Company, Waltham, Massachusetts, and Stechert-Hafner, Inc., New York, 1955. Pp. 262, plates 23, figs. 28. Price $7.50.

The author, who is professor of plant anatomy at Harvard University, has brought together in this volume such of his 113 published papers as would best illustrate the eight units into which he has seen fit to divide them. These units deal with cytology and ontogeny, biochemistry and biophysics, phylogeny, taxonomy, entomology, paleobotany, wood technology, and cooperation in scientific research. The book reviews the lifetime research and concepts of a well-trained and highly capable botanist whose first paper appeared in 1909. In his chapter on the role of research in the development of forestry in North America he discusses the empirical nature of much of the experimentation in soil science and plant physiology and points to the need that such work "should not be shackled by demands for practical application." A list of some 200 references is appended. The illustrations, including the headpieces and vignettes by B. G. L. Swaney, are exceptionally good. The book contains a great wealth of valuable information. It is volume 15 of Chronica Botanica.

Cotton Growing Problems. By Basil G. Christidis and George J. Harrison. McGraw-Hill Book Company, New York, 1955. Pp. 633, figs. 168. Price $9.75.

Professor Christidis is director of the Cotton Research Institute, Sindos, Greece, and his associate was formerly principal agronomist at the Cotton Field Station, Shafter, California. Together they have covered cotton-production problems as they are presented in most of the more important cotton-growing regions of the earth. The book is organized under varieties, rotations, fertilizers, seed, planting, culture, pests, and harvesting. A long list of references is appended to each of these eight divisions, the work of some 500 authors being mentioned in the book as a whole. The unique feature of the book is the coverage of the large numbers of technical papers that are scattered through the literature. Many of the data, however, are published for the first time. The illustrations are largely from the United States. Persons concerned with any phase of cotton research will find much of interest and value in this book.

A Dictionary of Terms in Pharmacognosy. By George Macdonald Hocking. Charles C. Thomas, Publisher, Springfield, Illinois. Pp. 284. Price $9.75.

Pharmacognosy has to do with medicinal products of plant, animal, and mineral origin. The author, who is a professor in the department of pharmacognosy at Alabama Polytechnic Institute, must have spent a great deal of time in the development of this highly interesting and useful book. Botanical, vernacular, phytochemical, technical, and pharmaceutical terms are defined. A list of 83 cited references and a considerable number of general references are appended, as well as terms describing properties and therapeutic uses of drugs. This is a first-class presentation of the subject, dealing with matters of much importance to soil-plant scientists. It is of interest to note that toddy is the sap of palms, that ragweeds have no known medicinal value, and that "koke" is a recognized word in the language of this country.

The Earth Beneath Us. By H. H. Swinnerton. Frederick Miller, Ltd., London, 1955. Pp. 320, figs. 28, plates 16. Price 21s net.

The author, professor emeritus of the University of Nottingham, presents his subject with the thought of its "peculiar educational and cultural value." He deals with the origin of the earth, its facial characteristics, the realm of Pluto, the climates of the past, the beginnings of life, and the coming of man. He starts with Joseph's dream in which the sun, moon, and 11 stars appeared before him, discusses the earliest of man's concepts of the earth and its heavenly surroundings, and then proceeds to develop a great variety of interesting and informative material on the evolutionary aspects of the earth and the life that exists on it.

Estudio Analitico de Complejo Coloidal Organico en Suelos Argentinos. By Maria Antoineta Servici de Rondini. Reprinted from *Revista de Investigaciones Agricolas* 8: 225–247, 1954. Buenos Aires, Argentina.

The author is chief of the microbiological and biochemical laboratory of the

Division of Edaphology, Institute of Soils and Agrotechnology, Ministry of Agriculture. The study has to do with humification in soils in relation to the various climatic zones of Argentina. It is concluded that soil organic matter is in part active and nutritional and in part resistant to decomposition; that the carbon content of the first is 35–40 per cent, whereas that of the second is 56–58 per cent; that the second contains lignin and protein in the ratio of approximately 2 to 1; and that the conventional carbon-organic matter factor 1.724 applies generally to soils having an organic matter content of less than 7 per cent.

Glossary of Selected Geologic Terms. By WM. LEE STOKES AND DAVID J. VARNES. *Colorado Scientific Society Proceedings.* Volume 16. Denver, Colorado, 1955. Pp. 165. Price $2.75, paper-bound; $3.50 cloth-bound.

The purpose of the authors is to provide engineers and other nongeology specialists with the explanations for terms commonly employed by geologists. The 2,670 entries include some of the simpler terms in mineralogy, paleontology, and soils, and of those in zoology that apply to fossils. The starting point is "aa," a Hawaiian word for a rough jagged, solidified lava. The final word is "zoogenic deposit," meaning a deposit formed through the agency of animals. Both nouns and adjectives are included, and an occasional prefix. The term "laterite" is made to include what is now termed "latosol." The definition for "caliche" does not include the Chilean nitrate salt deposits. But the book is interesting, useful, and constructive and should prove valuable to those who have need for it.

Humisol. By GEORGE F. CARTER AND V. P. SOKOLOFF. Reprinted from *Review of Geographical Institute of the University of Istanbul,* International Edition, 1954. Pp. 16, figs. 3.

The authors, who are associated with the Isaiah Bowman School of Geography, The Johns Hopkins University, "advance the hypothesis that there is fundamentally but one soil forming process in the humid lands of the world, and that the many soil types can be thought of as different time stages in the normal course of development that soils subject to this process undergo. We wish to emphasize process and time. We propose the name 'Humisol' for the product of this process." Eastern United States, from New England to Florida, was used as the test area.

Land Judging. By EDD ROBERTS. The University of Oklahoma Press, Norman, 1955. Pp. 120, plates 16. Price $2.50.

The author pioneered in the development of land-judging methods and contests and in the preparation of score cards for this purpose. At the time the book was published he had supervised 301 such contests in which some 62,000 persons had participated. He is particularly interested in 4-H Club members and in Future Farmers of America but believes that people of all ages, interests, and training find land-judging a highly rewarding thing to try. The book is divided into six units on importance of soil, judging by physical characteristics, by soil tests and classification, and by score card, conducting land-judging contests, and

implementing the contest. A glossary of terms is appended. The author has found his work highly rewarding and passes on his experiences to those who are in position to apply them, to the end that more persons learn to appreciate the nature of the soil and the need for its conservation.

Methods of Collecting Current Agricultural Statistics. By FOOD and Agricultural Organization of the United Nations. Columbia University Press, New York, 1955. Pp. 272. Price $3.

This report was prepared by R. D. Narain. The purpose is to present the methods employed in the several countries; to educate those concerned, to the end that improved methods are employed; and to supply fresh material as improved methods are put into operation.

Microbiology. By ERNEST GRAY. Philosophical Library, Inc., New York, 1955. Pp. 175, figs. 25. Price $3.75.

The author of this small volume is chief bacteriologist, Bayer's Biological Institute, Exning, England. The book is designed as an introduction to the subject. It covers the biology and culture of microorganisms, host-parasite relationships, viruses, bacteria, yeasts, fungi, algae and protozoa, microbiology of soil, inland waters, and the sea, and applications of microbiology. Included in the applications are foods, brewing, wine, silage, and flax retting. A list of 85 pertinent references and of 10 texts is appended. The book is pocket-sized. The type is small. The material is well presented, and the author makes some interesting supplemental comments.

Nutritional Disorders in Plants. By C. R. VON STIEGLITZ AND F. CHIPPENDALE. Department of Agriculture and Stock, Queensland, Australia, 1955. Pp. 36, color plates 36.

This bulletin illustrates, in color, symptoms of nutritional disorders. Included are deficiency symptoms for nitrogen in legumes and nonlegumes; phosphorus in cabbage and corn; potassium in alfalfa; calcium in tomato and oats; magnesium in cotton; boron in sweet potato, turnip, alfalfa, cauliflower, tobacco, and lemon; copper in lemon and pineapple; zinc in orange; molybdenum in lettuce, cucumber, tobacco, cauliflower, rose, and strawberry clover; iron in eucalyptus; and manganese in oats, pineapple, banana, bean, and peanut. Also shown are toxicity symptoms for chlorine in tobacco, boron in bean, and zinc in cabbage. In each case the signs, cause, and treatment are given.

The Only Way Out. By JACOB ROSIN. The American Press, New York, 1955. Pp. 114. Price $2.95.

The author calls for an investment of 30 billion dollars in research during the next 5 years. This would permit of a fivefold enlargement of the chemical industry within the next 10 years. And the task of this enlarged industry would be to eliminate the need for agriculture by replacing its products with synthetic foods and textiles. Farmers would be trained for industry. The Russians would be so far outdistanced by such a chemistic society as to be virtually helpless.

Pflanzenernährung und Bodenkunde. Seventh Edition. By KARL SCHMALFUSS. S. Hirzel Verlag, Leipzig, Germany, 1955. Pp. 304, figs. 27. Price D.M. 7.50.

The author is director des Instituts für Pflanzenernährung und Bodenkunde der Universität Halle. The changes in this edition are relatively minor. The book covers the origin of soils and their biological, physical, and chemical properties, the nutrition of plants, and the use of manures and fertilizers. It has special value in that it represents the current thinking of German workers in this field of study. All but two of the appended references are of German origin, the exceptions being J. Bonner's "Plant Biochemistry" and G. W. Robinson's "The Soil," translated into "Der Boden."

Plant Ecology. By United Nations Educational, Scientific, and Cultural Organization. Columbia University Press, New York, 1955. Pp. 377. Price $7, paper-bound; $8 cloth-bound.

This is a review of the literature on plant ecology with special reference to arid and semiarid regions in Afghanistan, Iran, Israel, Turkey, Latin America, Australia, Irak, Egypt, Union of South Africa, Northwest Africa, United States, Canada, and Tropical East Africa and other nearby arid countries. It has been developed by capable research workers in the several countries covered. Most of the material is presented in English with French résumés, but an occasional paper is in French. Extended bibliographies of as many as 600 references for a single paper are appended. Some interesting graphs and illustrations are contained in the report. A series of maps on Australian ecology is enclosed in an envelope attached to the back cover. Ecologists will want a copy of this book for frequent reference, and other soil-plant scientists will find it of much interest and value.

Proceedings of the American Society of Sugar Beet Technologists. Volume 8, Part 2. James H. Fischer, secretary, Fort Collins, Colorado, 1954. Pp. 459.

Development of a research program around a specific crop by representatives of industry and of state and federal research agencies has much merit. This is well illustrated in this report, which contains the papers presented at the eighth annual meeting, held at Denver, Colorado, February 2–5, 1954. Among the many worthwhile papers contained in this volume, those on factory waste disposal, nitrogen levels, mineral nutrients in relation to germination, water levels in relation to mineral nutrition, and nitrogen fertilization in relation to glutamic acid content of sugar beets are of particular interest to soil scientists. These papers were presented by Messrs. Hungerford, Ulrich, Snyder, Kelley, and Hac, respectively. An excellent paper on recent advances in the physiology and biochemistry of respiration, by Myron Stout, merits special mention.

Quantitative Spectrochemical Analysis of Silicates. By L. H. AHRENS. Addison-Wesley Publishing Company, Inc., Cambridge, Massachusetts. Pp. 122. Price $3.75.

Rapid improvement is being made in spectrochemical procedures for use in

the analysis of inorganic and biological materials. The author of this book, who is reader in mineralogy, Oxford University, has made highly important contributions to our knowledge in this field. In his book he presents a scheme of quantitative analysis for silicate minerals with the DC arc that can be applied to soils. He divides his subject into miscellaneous matters, standards, errors, alkalies, volatile and involatile groups, fluorine, and the common elements. Among the points emphasized is the necessity of having essentially the same chemical and physical properties in the standards as in the unknowns, or the importance of the matrix. He indicates that spectrochemical methods are far superior to chemical methods at low concentrations of an element like potassium. A bibliography of 100 references is appended. Every spectrographer will want a copy of this book close at hand.

Range Management. Second Edition. By LAURANCE A. STODDART AND ARTHUR D. SMITH. McGraw-Hill Book Company, Inc., New York, 1955. Pp. 433, figs. 156. Price $7.

The authors, who are associated with the department of range management of Utah State Agricultural College, have developed an excellent text on the art and science of range management. The chapters deal with the growth of the science, physical features of western range land, plant physiology, ecology, technical methods of research, inventory, natural fauna, timbered grazing land, poisonous plant problems, eradication of undesirable plants, reseeding, livestock management, range operations, and animal nutrition. It is of interest to note that this country once had 50 million bison, that we now have about 95 million cattle and 30 million sheep, and that we are consuming more than 140 pounds of beef, veal, mutton, lamb, and pork per person annually. We have only a little more than half as many cattle as has India and a little more than one fourth as many sheep as has Australia. Of our 1,904 million acres, 1,020 million are classified as grazing land. The book is well written and contains a large number of important facts and suggestions. The illustrations are excellent and are highly useful in understanding the text.

Report of the Rothamsted Experimental Station for 1954. Librarian, Rothamsted Experimental Station, Harpenden, 1955. Pp. 241, Price, paper-bound, 7/6, foreign postage extra.

The preface contains a short history of the Station from 1843 to date. Special mention is made of the work of the late E. M. Crowther, and a detailed list is given of his publications, comprising more than 100 papers. Among the many lines of study now under way at the Station are those dealing with the irrigation needs of England and Wales, minerals occurring in soil clays, use of antagonistic microorganisms to control root disease fungi, oxidizing enzyme systems, conditions favoring virus infection, iron-manganese relationships, nematode population buildup, manner of operation of organophosphorus insecticides, insect migration, social behavior of bees, and use of electronic computers in statistical analysis. In October, 1954, R. K. Scofield was put in charge of the chemistry

department and H. L. Penman of the physics department. A large number of field experiments are reported. Special reports are presented on soil survey of England and Wales, clay minerals, and uptake of nutrients from leaf sprays. A list of 201 publications is appended.

Report on the 1950 World Census of Agriculture. Volume 1. By Food and Agricultural Organization of The United Nations. Columbia University Press, New York, 1955. Pp. 160. Price $2.

This work is being published in installments. The price of the first volume includes a loose-leaf cover designed to bind the entire series of reports. The data in this volume are from 30 countries, not including England, France, Italy, Russia, or the United States. The data for some countries are much more complete than for others. It is of interest to note that of 48,000 persons in New Hebrides, 47,700 are dependent on agriculture; that Hawaii produces more than 7 million metric tons of sugar; and that the Republic of Germany grows only 9,483 hectares of maize.

Soil Warming by Electricity. By R. H. Coombes. Philosophical Library, New York, 1955. Pp. 116, plates 16. Price $4.75.

The author gives a history of soil-warming developments, discusses the early experiments, and then proceeds with a detailed consideration of modern electrical methods of soil warming, with costs and possible profits. In the second part of the book he deals in succession with applications in the production of vegetables, fruits, and flowers. It is of special interest to note the suggested use of John Innes Base, which consists of hoof and horn, two parts; superphosphate, two parts; and sulfate of potash, one part, all by weight. Mention is also made of the Chase Cloches, or little glass houses for use in growing early crops in the field. Those interested in the subject will find this book of considerable value.

Symposium on Permeability of Soils. American Society for Testing Materials, Philadelphia, 1955. Pp. 136, Price, paper-bound, $3 ($2.25 to members of ASTM).

The papers presented at the 57th Annual Meeting of the Society in Chicago, June 15, 1954, dealt with permeability testing; water movement through porous hydrophilic systems; low-head permeameter for testing granular materials; permeability test for sands; permeability of compacted fine-grained soils, sand, and sand-gravel mixtures; measurement of hydraulic conductivity of soil in place and of permeabilities in ground-water investigations; and determination of permeability of granular soil by air subjected to a decreasing pressure differential. A selected list of references is appended. Don Kirkham and Hans Winterkorn were among those who presented papers.

World Economic Geography. By Earl B. Shaw. John Wiley and Sons, Inc., New York, 1955. Pp. 582. Price $6.50.

After discussing the meaning of economic geography, the author divides his

subject into four units: forest, fish, and animal industries; agriculture; manufacturing and trade; and population. Soil-plant scientists will be especially interested in the sections on agriculture and population. Farming is discussed in terms of tropical rainforests, savannas, steppes, deserts, Mediterranean areas, humid subtropical regions, west-coast marine climates, humid continental lands, and subarctic regions. Appended to each chapter are questions, exercises, and problems and a list of selected references. The book is well written and well illustrated. The chapter on population contains an interesting distorted map in which the several countries are shown on a scale commensurate with their numbers of inhabitants. China and India are very large, whereas the U.S.S.R. and Africa are relatively small. The author has developed an excellent text, with helpful suggestions for further study.

Yearbook of Food and Agricultural Statistics. By Food and Agricultural Organization of The United Nations. Columbia University Press, New York, 1955. Pp. 347. Price $3.50.

This is part 2 of volume 8 of the series. The data are presented in English and French and the notes and glossary in Spanish as well. The table on balance of trade in food products is of special interest. The United States, for example, has a negative balance in meat, fish, sugar, coffee, feeding stuffs, and beverages, and a positive balance in dairy products and cereals. Informative notes on commodities of the various countries are appended.

THE EDITORS

Pochvovedenie. Second Edition. By D. G. VILENSKII. Gosudarstvennoe Uchebno-Pedagogicheskoe Izdatel'stvo Ministerstva Prosveshcheniya RSFSR (U.S.S.R.), Moscow, 1954. Pp. 456, plates 124.

This second edition was worked over "in the light of the problems confronted by science in implementing the directives of the 19th Congress of the Communist Party and the resolutions of the September (1953) and February–March (1954) plenary sessions of the Communist Party on means of advancing agriculture." All through the text the dark shadows of the official line, which Vilensku was forced to follow, obscure to the uninitiated the otherwise clear, interesting, and scholarly presentation of pedological principles and of the characteristics of zonal soils. For good measure, and probably to strengthen his reputation with the official line, Vilensku discusses the soils of the People's Democracies, which, "with the brotherly help of the Soviet Union, are developing their productive forces and building a socialistic people's economy." The volume contains maps of the soils of the world, of the U.S.S.R., and of China, Mongolian People's Republic, and Korea, and a map of the quaternary deposits of European Russia and adjacent regions. Six profiles are shown in color. No reference is made to the publications of the bourgeois world.

JACOB S. JOFFE

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DIFFUSION OF WATER VAPOR AND ITS EXCHANGE BETWEEN CONDENSATION AND EVAPORATION IN SOIL

HITOSHI FUKUDA

Faculty of Agriculture, University of Tokyo, Japan

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This paper concerns the quantitative change in diffusion of water vapor in relation to its condensation and evaporation in soil pores, as determined by measurements of daily fluctuations of temperature, relative humidity, and soil moisture at various depths in fields of loamy and sandy soils.

THEORY

Penman's[1] fundamental equation for water vapor movement in soil pores is

$$\frac{\partial v}{\partial t} = \frac{k_0}{\sqrt{2}} \cdot \frac{\partial^2 v}{\partial z^2} \qquad (1)$$

Therefore an increase of vapor in an infinitesimal unit volume of soil, in time dt, is

$$\frac{k_0}{\sqrt{2}} \cdot \frac{\partial^2 v}{\partial z^2} \cdot dt \qquad (2)$$

where v is the mass of vapor in the unit volume of soil (g./cc.), and $k_0/\sqrt{2}$ is taken as the coefficient of diffusion of water vapor (sq. cm./sec.), k_0 being the value in air. It will be demonstrated experimentally that v in expression (*2*) may be considered to be in equilibrium with the soil moisture w; v is known to be a function of w and the absolute temperature T. Therefore, the total increase of v due to an increase of dT in time dt may be expressed as

$$\frac{\partial v}{\partial T} \cdot \frac{\partial T}{\partial t} \cdot dt \qquad (3)$$

It will be shown experimentally that the increase (*3*) in amount of vapor is due to evaporation or condensation in soil pores, in which case the increase of dT is considered to include latent heat. If, therefore

$$\frac{\partial v}{\partial T} \cdot \frac{\partial T}{\partial t} > \frac{k_0}{\sqrt{2}} \cdot \frac{\partial^2 v}{\partial z^2}$$

evaporation occurs at time t and at height z, and the difference between these two terms corresponds to the amount of evaporation (g./cc./sec.). If

[1] PENMAN, H. L. Gas and vapor movements in the soil. *J. Agr. Sci.* 30: 437–462. 1940.

$$\frac{\partial v}{\partial T} \cdot \frac{\partial T}{\partial t} < \frac{k_0}{\sqrt{2}} \cdot \frac{\partial^2 v}{\partial z^2}$$

condensation takes place, and the amount of condensation corresponds to the difference between these two terms.

Now we can say that, approximately,

$$\rho_v = v/\mu$$

where μ = pore space (cc.) in a unit volume (cc.) of soil, and ρ_v = density of water vapor. Then

$$p = \frac{R}{M} \cdot T \cdot \rho_v = \frac{R}{\mu M} \cdot v \cdot T$$

and

$$p/p_s = h(w)$$

Here p = vapor pressure at temperature T, p_s = maximum vapor pressure at T, and $h(w)$ = relative humidity in soil pores. With R equal to the gas constant per gram molecule and M = the molecular weight of the water vapor

$$v = \frac{\mu M}{R} \cdot \frac{p_s}{T} \cdot h(w) \tag{4}$$

As $h(w)$ is virtually independent of temperature T, shown later in experiments,

$$\frac{\partial v}{\partial T} \cdot \frac{\partial T}{\partial t} \gtrless \frac{k_0}{\sqrt{2}} \cdot \frac{\partial^2 v}{\partial z^2}$$

becomes

$$\frac{d}{dT}\left(\frac{p_s}{T}\right) \cdot h \cdot \frac{\partial T}{\partial t} \gtrless \frac{k_0}{\sqrt{2}} \cdot \frac{\partial^2}{\partial z^2}\left(\frac{p_s}{T} \cdot h\right) \tag{5}$$

As a general check, let us consider two cases, one where relative humidity $h(w)$ is found equal to 1.00, and the other where it is found to be below 1.00, and the following equation for water vapor movement

$$\frac{\partial v}{\partial t} = \frac{k_0}{\sqrt{2}} \cdot \frac{\partial^2 v}{\partial z^2} + u \tag{6}$$

with u = mass of water evaporating in unit time, in pores of unit volume of soil (g./cc./sec.).

Case I: $h = 1.00$

In this case, vapor pressure p at any depth z, at any time t, and at any temperature T is equal to its maximum value p_s at the same temperature. From equation (*4*)

$$v = \frac{\mu M}{R} \cdot \frac{p_s}{T} \tag{7}$$

Considering equation (7) for a small time interval, we can find an interval during which the temperature is constant and consequently $\partial T/\partial t = 0$. Then $\partial v/\partial t = 0$. Equation (6) there becomes

$$u = -\frac{k_0}{\sqrt{2}} \cdot \frac{\partial^2 v}{\partial z^2} \tag{8}$$

and

$$\frac{\partial^2 v}{\partial z^2} = \frac{\mu M}{R} \frac{\partial}{\partial z}\left[\frac{d\left(\frac{p_s}{T}\right)}{dT} \frac{\partial T}{\partial z}\right] = \frac{\mu M}{R}\left[\frac{d^2\left(\frac{p_s}{T}\right)}{dT^2}\left(\frac{\partial T}{\partial z}\right)^2 + \frac{d\left(\frac{p_s}{T}\right)}{dT} \frac{\partial^2 T}{\partial z^2}\right] \tag{9}$$

If, from calculations based on experimental data, the sum of the two terms in brackets on the right-hand side of equation (9) is found to be positive, then, since $\mu M/R$ is positive, $\partial^2 v/\partial z^2$ must also be positive, and thus equation (8) will show u to be negative; that is, there will be condensation. Conversely, if $\partial^2 v/\partial z^2$ is found to be negative, u is greater than 0 and there will be evaporation.

Case II: $h < 1.00$

In this case, $p < p_s$ and evaporation is likely to occur, so u and p can be expressed as follows:

$$u = \alpha(p_s - p) \tag{10}$$

$$p = \frac{R}{\mu M} vT \tag{11}$$

Here α is a coefficient. When condensation occurs, $u < 0$, and just as condensation is about to set in

$$p_s = p = \frac{R}{\mu M} T \tag{11a}$$

Taking a steady state, $\partial T/\partial t = 0$, $\partial v/\partial t = 0$, and $v \propto p$, we get from equations (6), (10), and (11)

$$\frac{\partial p}{\partial t} = \frac{k_0}{\sqrt{2}} \cdot \frac{\partial^2 p}{\partial z^2} + \frac{RT\alpha}{\mu M}(p_s - p) = 0$$

With $p_s - p = y$, and $\dfrac{RT\alpha\sqrt{2}}{\mu M k_0} = \lambda^2$, we have

$$\frac{d^2 y}{dz^2} - \lambda^2 y = 0 \tag{12}$$

The boundary conditions for equation (12) are (fig. 1): $y = 0$ when $z = 0$; and $y = p_s - p_0$ when $z = l$, where p_0 is the vapor pressure at $z = l$. A solution of equation (12) is

$$y = (p_s - p_0)\frac{\sinh \lambda z}{\sinh \lambda l}$$

$$p = p_s - y = p_s - (p_s - p_0)\frac{\sinh \lambda z}{\sinh \lambda l}$$

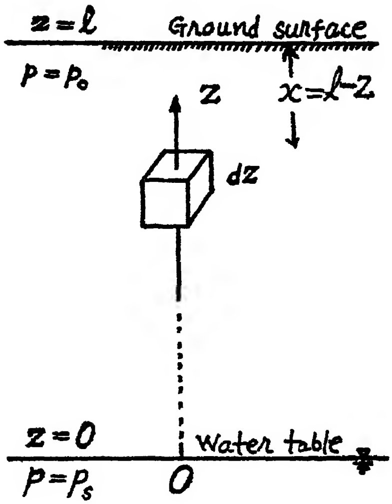

FIG. 1. MOVEMENT OF WATER VAPOR IN SOIL

TABLE 1

Size and total surface area of particles in a unit volume of soil

Diameter of soil particle . . . *cm.*	0.1	0.01	0.001	0.0001
A values............ *sq.cm/cc.*	59.690	596.90	5969.0	59690

If we let $l - z = x$

$$p = p_s - (p_s - p_0)[\cosh \lambda x - \coth \lambda l \cdot \sinh \lambda x] \tag{13}$$

and when $\lambda l \gg 1$

$$p = p_s - (p_s - p_0) \cdot e^{-\lambda x} \tag{14}$$

In equation (*14*), when $x = 1/\lambda$, $e^{-\lambda x} \doteqdot \frac{1}{3}$. Thus by calculating λ we can estimate the depth where vapor pressure depression from saturation is one third that at the ground surface.

To get an order of λ, we have to fix the value of the coefficient α in equation (*10*). From the molecular theory,[2]

$$u = A \sqrt{\frac{M}{2\pi RT}} (p_s - p) \tag{15}$$

$$\alpha = A \sqrt{\frac{M}{2\pi RT}} \tag{16}$$

where A is the total surface area of particles in a unit volume of soil from which evaporation arises, depending on $(p_s - p)$. If these particles are assumed to be a loosely packed sphere, the values of A in 1 cc. of soil are those shown in table 1.

[2] MAYER, J. E. AND MAYER, M. G. Statistical Mechanics. 1940.

By putting these values of A into equation (*16*), the coefficient α can be determined.

EXPERIMENTS

Two bare fields, one of loamy soil and the other of sandy soil, were used during a very dry period of summer for the experiments. The following measurements were made 10 times every 24 hours at each field:

At and above the ground surface, by means of a small Assmann's psychrometer: air temperature, relative humidity, and vapor pressure at heights of 0 (surface), 1.0, 5, 20, 50, and 100 cm.

At and below the ground surface, where the water table is at a greater depth than about 5 m. (a value λl in equation *13* will be about $10^5 \sim 10^7$, when l in figure 1 is 1 m., as shown in table 6): soil moisture at depths of 0, 3, 10, 20, and 30 cm., by an ordinary method of sampling and drying; soil temperature at 0, 3, 5, 10, 20, 30, and 50 cm., by a soil thermometer of rod type; and relative

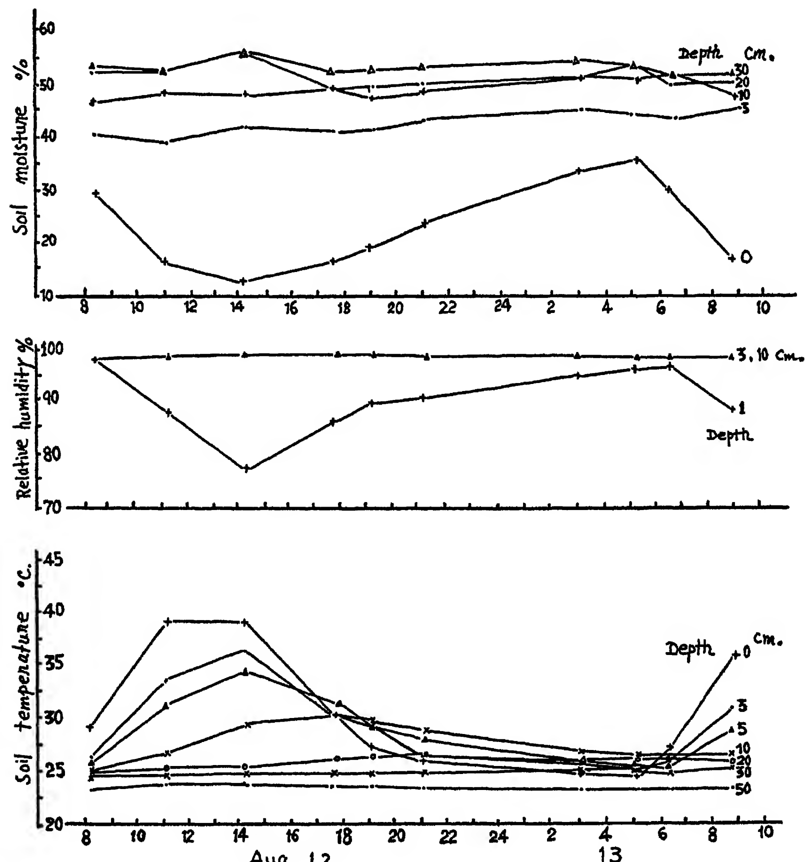

FIG. 2. CHANGE OF SOIL MOISTURE, RELATIVE HUMIDITY IN SOIL PORES, AND SOIL TEMPERATURE IN LOAMY FIELD

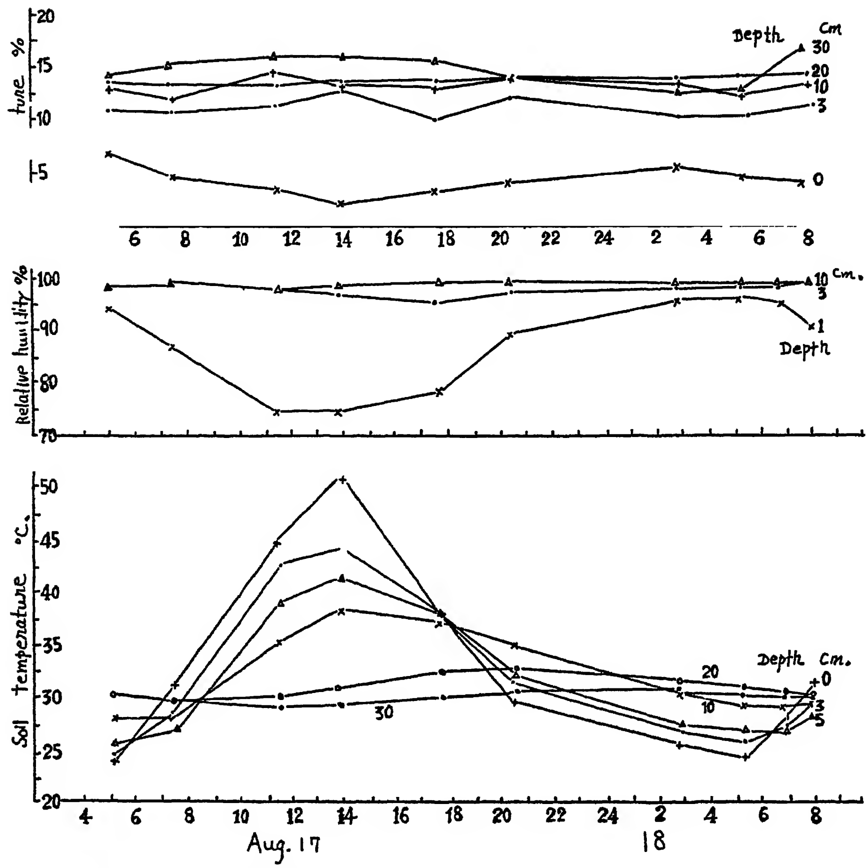

FIG. 3. CHANGE OF SOIL MOISTURE, RELATIVE HUMIDITY IN SOIL PORES, AND SOIL TEMPERATURE IN SANDY FIELD

humidity at 1, 3, and 10 cm., by the electrical hygrometer of the American Instruments Co.

The results of these measurements are shown in figures 2, 3, 4, and 5, and the figures reveal the following facts:

(*a*) The fluctuation of soil moisture within 24 hours shows, especially near the ground surface, a decrease in daytime and an increase at night. Since soil moisture in the two fields decreases toward the surface (figs. 2 and 3), the soil moisture curve shows an upward trend. It has been shown[3] that at night moisture accumulates near the surface and the water content increases as a result of vapor condensation there.

(*b*) The fluctuation of relative humidity, when below 100 per cent in soil pores within a 24-hour period is similar to that of soil moisture. Near the surface

[3] FUKUDA, H. Studien über die elektrische Bodenwasserbestimmung im Felde und den Einfluss des Regenfalles auf das Bodenwasser. *J. Coll. Agr., Tokyo Imp. Univ.* 14: 287–375. 1937.

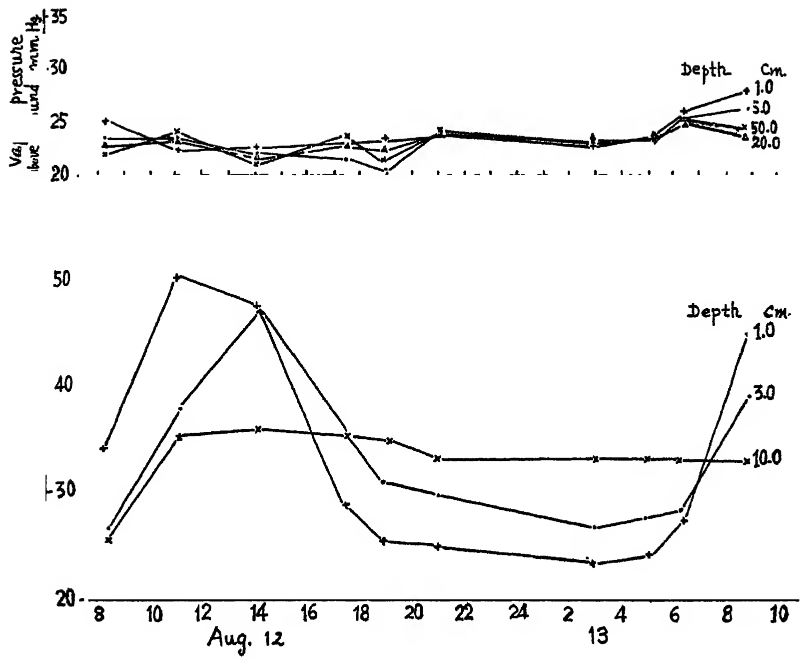

FIG. 4. CHANGE OF WATER VAPOR PRESSURE ABOVE AND BELOW THE GROUND SURFACE IN LOAMY FIELD

its minimum appears at about 2 p.m. and its maximum at about 6 a.m. (figs. 2 and 3). In the sandy field the fluctuation at a depth of just 3 cm. shows some time lag when compared with that of the surface where relative humidity in soil pores, since it depends on soil moisture content near the surface, is not always equal to 100 per cent even at night.

(*c*) The relation between soil moisture and relative humidity in soil pores in the two fields is shown in figure 6. Curves 1 and 2 were derived from data obtained in a desiccator with various concentrations of dilute H_2SO_4 in equilibrium; the plots indicate data observed in the fields. Since these two groups of plots lie close to the two curves, respectively, the field measurements of soil moisture and relative humidity are considered to have been made in equilibrium. In addition, considering that the experiments with a desiccator were made at a temperature between 15° and 35°C. and the field experiment temperatures (figs. 2 and 3) show rather wide fluctuations, the curves representing the relationship between soil moisture and relative humidity can be said to coincide fairly closely. Relative humidity below 100 per cent depends principally on soil moisture and little, if any, on soil temperature, though this has an influence on the vapor pressure itself; this point is explained somewhat by Schofield's[4] formula derived theoretically.

[4] SCHOFIELD, R. K. The pF of the water in soil. *Trans. Third Intern. Congr. Soil Sci.* 2: 39. 1935.

(*d*) In the daytime, vapor pressure in soil is highest at ground surface and much higher than that in the air above the surface. It can be concluded, therefore, that vapor moves both upward and downward from the ground surface. At night, on the other hand, vapor pressure in soil is lowest at ground surface; although it induces an upward movement in the soil, the movement into the air above the ground dependent, of course, on pressure difference, is almost negligible.

Both terms of equation (5) were calculated from data in figures 2 and 3 for morning, afternoon, and night, and are shown in table 2 at depths of 1, 3, and 10 cm. below ground surface, where p_s (g./sq. cm.), t (sec.), k_0 (sq. cm./sec.), z (cm.), and T in absolute temperature are used.

For example, let us make a calculation from the figures given in one row of

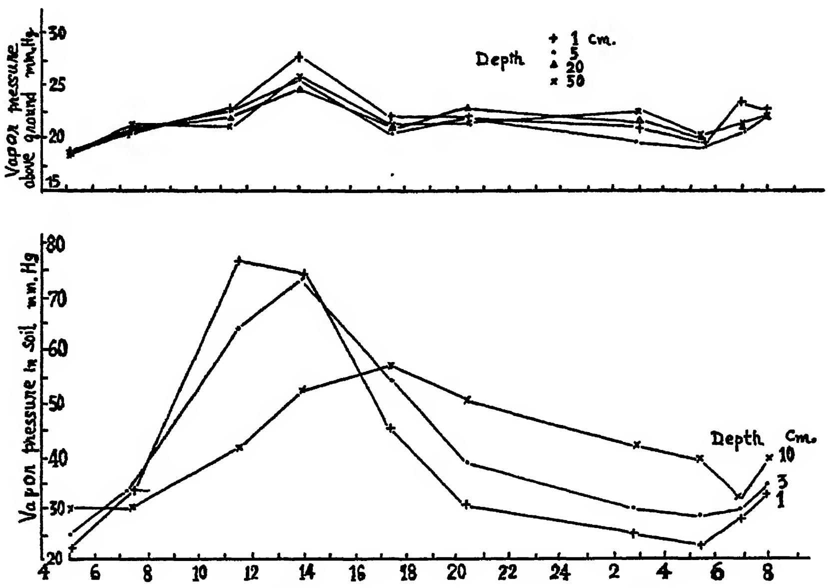

FIG. 5. CHANGE OF WATER VAPOR PRESSURE ABOVE AND BELOW THE GROUND SURFACE IN SANDY FIELD

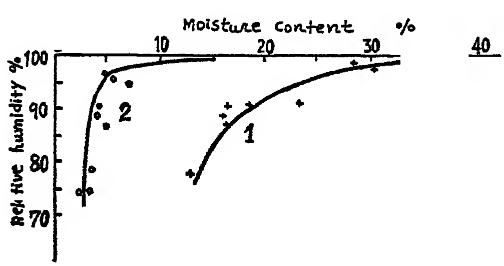

FIG. 6. RELATION BETWEEN SOIL MOISTURE AND RELATIVE HUMIDITY IN SOIL PORES: 1, IN LOAMY FIELD; 2, IN SANDY FIELD

TABLE 2

Relation between diffusion of vapor in soil and evaporation and condensation

Loamy Field						Sandy Field					
Time	Depth	$\frac{d}{dT}\left(\frac{p_s}{T}\right)\cdot h\cdot\frac{\partial T}{\partial t}$		$\frac{k_0}{\sqrt{2}}\cdot\frac{\partial^2}{\partial z^2}\left(\frac{p_s}{T}h\right)$	Remarks*	Time	Depth	$\frac{d}{dT}\left(\frac{p_s}{T}\right)\cdot h\ \frac{\partial T}{\partial t}$		$\frac{K_0}{\sqrt{2}}\cdot\frac{\partial^2}{\partial z^2}\left(\frac{p_s}{T}h\right)$	Remarks
	cm.						*cm.*				
9:37 a.m.	1	0.882×10^{-5}	>	-1.34×10^{-2}	E	9:27 a.m.	1	0.815×10^{-5}	>	-1.36×10^{-2}	E
	3	0.546×10^{-5}	<	0.0748×10^{-2}	C		3	0.923×10^{-5}	>	-0.27×10^{-2}	E
	10	0.1076×10^{-5}	<	0.0091×10^{-2}	C		10	0.400×10^{-5}	<	0.0113×10^{-2}	C
2:00 p.m.	1	0	>	-1.30×10^{-2}	E	2:00 p.m.	1	0	>	-4.87×10^{-2}	E
	3	0	>	-0.311×10^{-2}	E		3	0	>	-0.122×10^{-2}	E
	10	0.136×10^{-5}	<	0.028×10^{-2}	C		10	0	<	0.0294×10^{-2}	C
7:55 p.m.	1	-0.108×10^{-5}	<	0.183×10^{-2}	C	11:22 p.m.	1	-0.1105×10^{-5}	>	-0.164×10^{-2}	E
	3	-0.209×10^{-5}	>	-0.111×10^{-2}	E		3	-0.141×10^{-5}	>	-0.0744×10^{-2}	E
	10	-0.0912×10^{-5}	>	-0.0093×10^{-2}	E		10	-0.1635×10^{-5}	>	-0.0189×10^{-2}	E

* E = Evaporation; C = Condensation.

table 2: observations in a loamy field made at 9:37 a.m. at a depth of 3 cm. From figure 2 we find that the observed temperature at 8:15 a.m. was 26.4 + 273, and at 11:00 a.m., 33.5 + 273. The temperature at 9:37 a.m. was 29.9 + 273 and the relative humidity (h) was 0.985. With $\Delta T = 7.1$, and $\Delta t = 9.9 \times 10^3$, $\Delta T/\Delta t = 0.72 \times 10^{-3}$ and, from a physical table,

$$\frac{d}{dT}\left(\frac{p_s}{T}\right) = 0.77 \times 10^{-}$$

then

$$\frac{d}{dT}\left(\frac{p_s}{T}\right) h \cdot \frac{\partial T}{\partial t} = 0.564 \times 10^{-5}.$$

On the other hand, from a physical table, $k_0/\sqrt{2} = 0.1868$ and $p_s/T = 14.2 \times 10^{-2}$ and, using a graph of vertical distribution of $((p_s/T)\cdot h)$ near 3 cm. depth,

$$\frac{\partial^2}{\partial z^2}\left(\frac{p_s}{T}\cdot h\right) = 0.4 \times 10^{-2}.$$

Therefore

$$k_0/\sqrt{2}\cdot\frac{\partial^2}{\partial z^2}\left(\frac{p_s}{T}h\right) = 0.0748 \times 10^{-2}.$$

In table 2, the change of vapor induced by temperature change is

$$\frac{d}{dT}\left(\frac{p_s}{T}\right)\cdot h\frac{\partial T}{\partial t},$$

in which

$$\frac{d}{dT}\left(\frac{p_s}{T}\right)\cdot h > 0.$$

An increase or a decrease of vapor, therefore, depends on the sign of $\partial T/\partial t$. In the daytime, when $\partial T/\partial t > 0$, vapor increases, and at night when $\partial T/\partial t < 0$, it decreases. And the change in vapor by diffusion, expressed by

$$\frac{k_0}{\sqrt{2}}\frac{\partial^2}{\partial z^2}\left(\frac{p_s}{T}h\right.$$

in which $k_0/\sqrt{2} > 0$, depends on the sign of

$$\frac{\partial^2}{\partial z^2}\left(\frac{p_s}{T}h\right.$$

if the sign is negative, vapor decreases. As shown in table 2, in an absolute value the change induced by temperature has an order of 10^{-5}, and the change by diffusion 10^{-2}; in other words, the change in vapor by diffusion is exceedingly large.

At 9:37 a.m., evaporation near the ground surface of the loamy and sandy

fields is marked; it induces some increase in vapor to supply the decrease by diffusion. In other words, increase by evaporation is greater than decrease by diffusion. In the sandy field the same condition is observed at a depth 3 cm., but at all other depths in both fields, the decrease of vapor by condensation suppresses somewhat the increase by diffusion; as a result here the decrease by condensation is less than the increase by diffusion.

At 2 p.m., both at the ground surface and at a depth of 3 cm., in both fields the increase of vapor by evaporation is equal to the decrease by diffusion, the amount evaporated being completely carried away by diffusion. Condensation still takes place at a depth of 10 cm. At this depth in the loamy field, condensation is less than increase by diffusion; in the sandy field, condensation is being balanced by increased diffusion, or, in other words, condensation equals increase by diffusion.

By 7:55 p.m., condensation near the ground surface of the loamy field has already begun and, in spite of vapor increase by diffusion, there is a decrease in amount of vapor. Condensation in this case is greater than increase by diffusion. At the surface of the sandy field, and at all other depths in both fields, however, evaporation eventually becomes less than decrease by diffusion.

When the absolute value of

$$\frac{k_0}{\sqrt{2}} \cdot \frac{\partial^2}{\partial z^2} \left(\frac{p_s}{T} h \right)$$

is greater than that of

$$\frac{d}{dT} \left(\frac{p_s}{T} \right) h \frac{\partial T}{\partial t},$$

condensation occurs when the former is positive, and evaporation when it is negative.

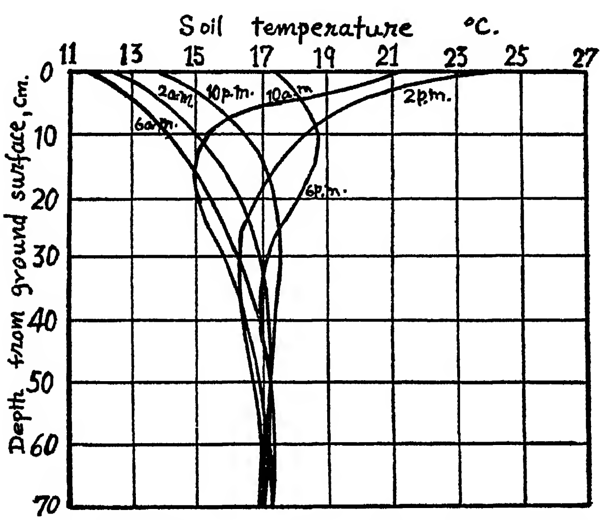

FIG. 7. CHANGE IN VERTICAL DISTRIBUTION OF SOIL TEMPERATURE WITH TIME

In respect to movement of water vapor in soil, it is understood that, in the daytime evaporation first appears near the ground surface, and the layer in which evaporation occurs gradually increases in depth. During this time condensation is still taking place in the lower layer. At night, with falling temperatures, condensation at the surface begins, and the layer of condensation increases in depth, following the path of the earlier evaporation layer.

Water vapor change where relative humidity h = 1.00

Let us now consider these relationships in the case of a relative humdity h of 1.00 by calculating $\partial^2 v/\partial z^2$ in equation (*9*), with soil porosity $\mu = 0.5$, $M = 18$ g./mol., $R = 8.314 \times 10^7$ erg./°K. mol. and other factors remaining the same. Examples of vertical distribution in soil temperature were taken at 6 a.m., 10 a.m., and 2 p.m. (fig. 7), in which the depth range with a great fluctuation of soil temperature was considered to be 30 cm. The point $z = 0$ is at this depth,

TABLE 3

Change of water vapor in soil pores at 6 a.m.

z	T-273	$\partial T/\partial z$	$\partial^2 v/\partial z^2$	k_0	$u = -k_0/\sqrt{2}\cdot\partial^2 v/\partial z^2$
30	11.89	—	—	—	—
27	13.07	−0.2983	-0.2093×10^{-11}	0.239	0.3537×10^{-11}
24	13.68	−0.1817	-0.4686×10^{-11}	0.2395	0.7938×10^{-12}
21	14.16	−0.1516	-0.1640×10^{-11}	0.240	0.2783×10^{-12}
18	14.59	−0.1350	-0.1778×10^{-11}	0.241	0.3030×10^{-12}
15	14.97	−0.1183	-0.1905×10^{-11}	0.2415	0.3254×10^{-12}
12	15.30	−0.1050	-0.1047×10^{-11}	0.2420	0.1791×10^{-12}
9	15.60	−0.0958	-0.9368×10^{-12}	0.2425	0.1607×10^{-12}
6	15.85	−0.0833	-0.1073×10^{-11}	0.2430	0.1843×10^{-12}
3	16.10	−0.0700	-0.1061×10^{-11}	0.2435	0.1827×10^{-12}
0	16.29	—	—	—	—

TABLE 4

Change of water vapor in soil pores at 10 a.m.

z	T-273	$\partial T/\partial z$	$\partial^2 v/\partial z^2$	k_0	$u = -k_0/\sqrt{2}\partial^2 v/\partial z^2$
30	21.00	—	—	—	—
27	17.64	0.7850	11.64×10^{-11}	0.2455	-2.021×10^{-11}
24	16.29	0.3575	2.905×10^{-11}	0.2440	-0.5011×10^{-11}
21	15.49	0.2017	1.808×10^{-11}	0.2425	-0.3101×10^{-11}
18	15.08	0.0825	1.629×10^{-11}	0.2415	-0.2782×10^{-11}
15	15.0	0.0033	0.6169×10^{-11}	0.2415	-0.1054×10^{-11}
12	15.06	−0.0366	0.4446×10^{-11}	0.2415	-0.7594×10^{-12}
9	15.22	−0.0616	0.2311×10^{-11}	0.2420	-0.3954×10^{-12}
6	15.43	−0.0766	0.1933×10^{-11}	0.2420	-0.3307×10^{-12}
3	15.68	−0.0950	0.3395×10^{-11}	0.2425	-0.5822×10^{-12}
0	16.00	—	—	—	—

TABLE 5

Change of water vapor in soil pores at 2 p.m.

z	T-273	$\partial T/\partial z$	$\partial^2 v/\partial z^2$	k_0	$u = -k_0/\sqrt{2}\cdot\partial^2 v/\partial z^2$
30	26.00	—	—	—	—
27	21.47	1.0900	18 79 $\times 10^{-11}$	0.2515	-3.341×10^{-11}
24	19.45	0.5330	5.399×10^{-11}	0.2485	-0.9486×10^{-11}
21	18.27	0.3130	2.756×10^{-11}	0.2470	-0.4815×10^{-11}
18	17.57	0.1860	1.497×10^{-11}	0.2455	-0.2599×10^{-11}
15	17.15	0.1200	0.4278×10^{-11}	0.2450	-0.07409×10^{-11}
12	16.85	0.0900	0.3101×10^{-11}	0.2445	-0.05362×10^{-11}
9	16.61	0.0666	0.3941×10^{-11}	0.2440	-0.06798×10^{-11}
6	16.45	0.0433	0.2901×10^{-11}	0.2440	-0.05004×10^{-11}
3	16.35	0.0250	0.2385×10^{-11}	0.2440	-0.04114×10^{-11}
0	16.30	—	—	—	—

the positive direction being upward. The results of these measurements are shown in tables 3, 4, and 5, and the figures reveal the following facts:

At 6 a.m. (table 3) $\partial^2 v/\partial z^2$ was less than zero, and u was greater than zero, or, by equation (*8*), evaporation arose in soil pores. Since dT/dz is greatest at the surface when it is a negative quantity, and since the diffusion coefficient (k_0) is almost constant, not only will the amount of vapor going out from one unit volume of soil be larger than the amount coming in, but there will also be a decrease of vapor. But because of a steady state $dT/dt = 0$ and $dv/dt = 0$, evaporation will have to arise in soil pores. This is evident (table 2), below the 3-cm. depth at night when the temperature of the soil is the same as it is at 6 a.m. (table 3).

By 10 a.m., when $\partial^2 v/\partial z^2$ has become greater than zero and u less than zero, condensation appears in soil pores. In the 10 a.m. curve (fig. 7) from the lowest temperature point water vapor moves upward as well as downward, indicating thereby that an increase of vapor in a unit volume of soil is taking place. But because of the steady state, condensation arises. The same soil temperature is seen at 9:37 a.m. (table 2), when, with relative humidity nearly 100 per cent, condensation at a depth is found.

At 2 p.m., $\partial^2 v/\partial z^2$ is greater than zero and u is less than zero, as was the case at 10 a.m. And as at 10 a.m., there is condensation in soil pores; with a relative humidity below 100 per cent, condensation at a depth is found (table 2).

Although some assumptions are made in the foregoing discussion, the relationship between evaporation, condensation, and diffusion of water vapor in soil pores is nevertheless evident when the vertical distribution of soil temperature is slowly changing with time, and the quantity of soil moisture sufficient for 100 per cent relative humidity.

Water vapor change where relative humidity h < 1.00

Now, to obtain the degree to which soil pores are saturated with water vapor assuming a steady state and a relative humidity below 100 per cent, the value of $1/\lambda$ in equation (*14*) must be calculated.

TABLE 6

Depth below the ground surface, at which vapor pressure depression from saturation is one third that at the surface

T	$\sqrt{\frac{M}{2\pi R}} \cdot \frac{1}{\sqrt{T}}$	k_0	$x = 1/\lambda$ cm.			
			Diameters of particles			
			0.1 cm.	0.01 cm.	0.001 cm.	0.0001 cm.
283	0.1103×10^{-4}	0.234	0.3101×10^{-3}	0.9804×10^{-4}	0.3101×10^{-4}	0.9804×10^{-5}
287	0.1096×10^{-4}	0.240	0.3128×10^{-3}	0.9891×10^{-4}	0.3128×10^{-4}	0.9891×10^{-5}
291	0.1088×10^{-4}	0.246	0.3157×10^{-3}	0.9980×10^{-4}	0.3157×10^{-4}	0.9980×10^{-5}
295	0.1081×10^{-4}	0.252	0.3184×10^{-3}	1.0067×10^{-4}	0.3184×10^{-4}	1.0067×10^{-5}
299	0.1073×10^{-4}	0.258	0.3211×10^{-3}	1.0155×10^{-4}	0.3211×10^{-4}	1.0155×10^{-5}
303	0.1066×10^{-4}	0.264	0.3238×10^{-3}	1.0240×10^{-4}	0.3238×10^{-4}	1.0240×10^{-5}

Values of $1/\lambda$ shown in table 6, in relation to various diameters of soil particles were derived from data in figure 7. From table 6 we observe that when the temperature of the soil is constant, the depth below the ground surface can be estimated to be $10^{-3} \sim 10^{-5}$ cm., depending on the diameter of soil particle, where vapor pressure depression from saturation is one third that at the ground surface, the depth increasing with the diameter of soil particle. Since this depth is exceedingly small, we may assume that, in a steady state, soil pores are virtually saturated with water vapor up to the ground surface.

In the calculation of the total surface area (A) of particles in a unit volume of soil (equation *16*), an ideal soil with loosely packed spheres was considered in the experiment. In a practical soil, however, not only are particles closely packed but smaller particles occupy the pores spaces in larger ones, thus increasing the value A, the coefficient α, and the value λ which makes the depth x decrease. Here, fundamental considerations, that is, an assumed steady state of soil temperature and no allowance for evaporation upward from the ground surface into the air, seem to account for the fact that the value $1/\lambda$ is so small. Actually in the loamy and sandy fields shown in figures 2 and 3, evaporation takes place from the soil surface and thus to some depth relative humidity is kept below 100 per cent.

SUMMARY

This paper deals with theoretical and experimental aspects of the process of water vapor diffusion in soil, in relation to evaporation and condensation in soil pores.

In two fields of loamy and sandy soils, measurements of air temperature, relative humidity, and vapor pressure were made both in daytime and nighttime at various heights above the ground surface. At the same time observations were made, at various depths, of soil moisture, soil temperature, and relative humidity in soil pores.

From these experiments, two major conclusions were drawn: (*a*) Relative humidity in soil pores, when below 100 per cent, shows a fluctuation within a

24-hour-period comparable to that of soil moisture; and as the depth below the ground surface increases, some time lag in this fluctuation occurs. (*b*) The amount of water vapor in soil pores depends on the degree of diffusion, evaporation, and condensation there, and the exchange involved in these processes.

And in respect to vapor movement in soil, evaporation in the daytime first appears near the ground surface, and the layer in which evaporation is observed gradually increases in depth, while condensation is still taking place in the lower layer. At night, when temperature drops, condensation begins at the ground surface and the layer increases downward following the same path as that of the evaporation layer.

CATION-EXCHANGE CAPACITY OF ROOTS AND ITS RELATION TO CALCIUM AND POTASSIUM CONTENT OF PLANTS

R. L. SMITH AND A. WALLACE

University of California, Los Angeles[1]

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The purpose of this investigation was to obtain information on the observed influences of citrus rootstocks on the scion. Previous workers (1, 7, 8, 9, 17, 19) noted rootstock differences in inorganic composition of leaves and other plant parts. Wallace *et al.* (19)[2] reported that, regardless of the scion species, some rootstock differences in inorganic composition of the leaves were consistent for rootstocks. The basis of the present investigation was one of the several possible reasons suggested by those investigators for the observed influences of rootstock on scion composition, namely, the differential ability of the roots to absorb nutrients. Because of the increasing volume of literature on the importance of the cation-exchange capacity of plant roots to cation absorption by plants, this factor was considered in the studies.

It has been shown that plant roots exhibit cation-exchange properties (3, 4, 5, 6, 10, 11, 13, 14, 15, 16, 18, 20). Williams and Coleman (20) showed that roots exhibit a "suspension effect," which indicates an ionic double layer. The H ions of H-saturated roots could be replaced by the cations of a neutral salt. Mattson and co-workers (4, 13, 14) determined the "acidoid strength" of plant roots and concluded that the root, which exhibits a colloidal nature, competed with the clay particles for cations and set up a Donnan equilibrium condition that governed the relative uptake of monovalent and divalent cations. The distribution of monovalent ions, such as those of KCl, in a system where two solutions are separated by a membrane and where there is a nondiffusible anion on one side of the membrane, would lead to a Donnan equilibrium state. This condition may be expressed as:

$$X_{\mathrm{Cl}} \cdot X_{\mathrm{K}} = Y_{\mathrm{Cl}}\,(Y_{\mathrm{K}} + Z_{\mathrm{K}}) \tag{1}$$

or

$$\frac{X_{\mathrm{Cl}}}{Y_{\mathrm{Cl}}} = \frac{(Y_{\mathrm{K}} + Z_{\mathrm{K}})}{X_{\mathrm{K}}}$$

where X is the activity of the anions and cations of the free salt in one solution (the "outside" solution), Y their activity in the "inside" solution, and Z the activity of the cation in combination with the nondiffusible anion. For $CaCl_2$ the distribution would be:

$$X^2_{\mathrm{Cl}} \cdot X_{\mathrm{Ca}} = Y^2_{\mathrm{Cl}}\,(Y_{\mathrm{Ca}} + Z_{\mathrm{Ca}}) \tag{2}$$

[1] The senior author's present address is Agronomy Department, Utah State Agricultural College, Logan.

[2] Note also "Rootstock influence on the magnesium nutrition of citrus," now in preparation by A. Wallace.

or

$$\frac{X_{Cl}}{Y_{Cl}} = \frac{\sqrt{Y_{Ca} + Z_{Ca}}}{\sqrt{X_{Ca}}}$$

Thus:

$$\frac{Y_K + Z_K}{X_K} = \frac{\sqrt{Y_{Ca} + Z_C}}{\sqrt{X_{Ca}}} \tag{3}$$

If the "outside" solution contained both $CaCl_2$ and KCl, a dilute solution would favor the accumulation of Ca over K, whereas in a more concentrated solution there would be little difference in accumulation of monovalent or divalent cations. Mattson (13, 14) extended the theory to include the "acidoid strength" of the plant roots as a determining factor in differential cation uptake. This acidoid or colloid is assumed to be the nondiffusible anion of the Donnan theory. The greater the acidoid strength of the roots, the greater will be the divalent cations adsorbed in proportion to monovalent cations at low ionic concentrations (4). Conversely, when the acidoid strength is low, the plant-root colloids should take up relatively more monovalent than divalent cations.

Drake *et al.* (3), in a study of the cation-exchange capacity of a number of agricultural plants and weeds, showed that the dicotyledons had a cation-exchange capacity nearly twice that of the monocotyledons. They used this finding in connection with Mattson's theory to explain why, under conditions of low soil K, grasses compete with associated legumes for K to the extent that legume yields and longevity are reduced. Later, Gray *et al.* (6) showed that when a legume and a grass were grown in association, the K uptake by plant species was closely correlated with the cation-exchange capacity of their roots. Grasses were rated as to their compatibility with Ladino clover on the basis of how they "crowded out" the legume. This rating corresponded to the cation-exchange capacities of their roots, that is, the grass with the lowest cation-exchange capacity was least compatible (bentgrass), whereas bromegrass, with the highest cation-exchange capacity, was the most compatible since it did not compete with the legume for K.

MATERIALS AND METHODS

The cation-exchange capacity (C.E.C.) of excised roots of various plants was obtained by the method of Drake *et al.* (3) as modified by Smith and Wallace (18). The surface area of some roots was determined prior to electrodialysis by selecting roots on which the diameter and length could be measured. After electrodialysis and titration, the dry weight was obtained; the C.E.C. was obtained on an area and a weight basis.

The plants studied were citrus and avocado species and representatives of herbaceous monocotyledons and dicotyledons. The citrus species used were rough lemon (*Citrus limon*), sour orange (*C. aurantium*), Blackman sweet orange (*C. sinensis*), L. V. W. Brown grapefruit (*C. paradisi*), and Rubidoux trifoliate orange (*Poncirus trifoliata*). Mexicola and Hass varieties of Mexican and Guate-

malan races of avocado (*Persea americana*) were used. The herbaceous plants were Atlas barley (*Hordeum vulgare*) and Six-Weeks Bountiful Bush beans (*Phaseolus vulgaris*). Limited tests were also run on excised roots of cuttings of peach (*Prunus persica*).

Cation-exchange capacities of roots of field-grown citrus seedlings (3 years old) and of large avocado trees were determined for comparison with those of roots from seedlings and cuttings grown in the glasshouse. Beans and barley were grown on washed silica sand and were 10 to 14 days old when the exchange capacity of the roots was determined. Except for the avocado seedlings grown in solution culture, the glasshouse plants received only tap water.

RESULTS AND DISCUSSION

Characteristics of cation-exchange capacity of roots

As noted by Drake *et al.* (3) there was a continual release of H from H-saturated roots when titrated with KOH. An initial large release of H by the KCl-replacing solution indicated an instantaneous surface reaction (20). The addi-

TABLE 1

Cation-exchange capacity of excised roots of various plant species

Plants	Cation-Exchange Capacity of Roots	
	me./100 g.	*me./sq. m.*
Rough lemon		
Trees*	30	
Seedling†	54	5.60
Sour orange		
Trees*	25	
Seedling†	45	5.19
Sweet orange		
Trees*	23	
Seedling†	40	5.12
Grapefruit		
Trees*	21	
Seedling†	49	5.09
Trifoliate orange		
Trees*	32	
Seedling†	54	5.72
Mexican avocado		
Tree‡—small roots	8.4	3.44
Tree‡—large roots	3.9	3.21
Mexicola seedlings§	12.6	2.42
Guatemalan avocado—Hass seedling§	27.6	2.08
Peach—rooted cutting	24.5	2.72
Barley—2 weeks old	23.3	0.77
Beans—12 days old	53.3	2.47

* Seedling trees in orchard—3 years old.

† Seedlings in glasshouse—7 weeks old.

‡ From large Hass on Mexican rootstock in orchard—15 years old.

§ Seedlings in solution culture—3 months old.

tional H, which is included in the values reported herein, was released only after the first H released had been neutralized. Such a release would follow if the exchange sites were weakly dissociated acids (16) and the degree of dissociation was highly variable. Marshall and Upchurch (15) have pointed out that since many colloidal systems are polyfunctional, it would be hard to make any significant estimate of the most difficultly replaceable H.

The C.E.C. of excised roots of a number of plants are given in table 1. Although the values obtained for roots of field-grown citrus trees were approximately half those obtained for roots of the same species grown in the glasshouse (7 weeks old), the relative differences between any two species were the same. The roots of the various citrus trees were somewhat larger and better developed than the fine fibrous roots obtained on the young seedlings in the glasshouse. When the areas of these fibrous roots were determined about the same relative differences in C.E.F. were found between species.

The values for root C.E.C. obtained for large and small roots of avocado trees give a striking example of what can result if the weight basis is used without caution, and why it is desirable to express the results on a surface basis. The large roots (2.5–4.0 mm. diameter) had about half the C.E.C. of the small roots (1.0–1.2 mm. diameter) when expressed on a weight basis, but no differences were found between the large and small roots when the C.E.C. was related to the surface area of the root.

Excised roots of newly rooted cuttings of peach were found to be very similar in exchange characteristics to roots of avocado seedlings, but quite different from any of the roots of the various citrus species. The roots of the herbaceous plants were markedly different from the roots of any of the tree species examined, in that they were fleshy with very little dry matter. When expressed on a weight basis, the C.E.C. of beans was comparable to that of the fine roots of citrus, whereas the C.E.C. of barley was more nearly like that of fine roots of avocados. Compared on an area basis, however, such similarities did not exist.

Obviously comparisons of root C.E.C. of a number of such varied plant species as those shown in table 1 should be expressed on a surface area basis. But if care is taken in selecting roots of comparable size, then comparisons on a weight basis is valid within broad groups, such as the citrus species or probably all the tree species considered here, and within the herbaceous plant group. The fact that it is easier to determine dry weight than to obtain the surface area of excised roots, makes a good argument for the use of the former. The root C.E.C. comparisons given in this paper were made on the weight basis.

Two experiments were conducted to determine (*a*) the influence of metabolic activity on the C.E.C. of excised roots, and (*b*) the portion of the root with the greatest exchange capacity. Like other roots (12), the tips of citrus roots were found to be more active in respiration than were segments farther back. Roots of sweet orange seedlings were segmented into 1-cm. sections and on a portion of each sample C.E.C. and respiration rate were each determined. When the H that was produced metabolically during the short titration time was subtracted from the total H neutralized, no difference in exchange characteristics was found

TABLE 2

Exchange properties of sections of roots of 2-month-old citrus seedlings and the effect of metabolic activity on exchange capacity

Root Sections	Cation-Exchange Capacity	
	Total	Corrected*
	me./100 g.	*me./100 g.*
Sweet orange:		
1st cm	41	37
2nd cm	37	36
3rd cm	38	36
Rough lemon (3-cm. sections):		
Alive at 26°C	49	
Alive at 0°C	51	
Dead at 26°C.†	50	

* Corrected by subtracting the metabolically produced H from total H.

† Soaked in ether for 1 hour.

between the tip and the third centimeter (table 2). As shown by Williams and Coleman (20), the exchange characteristics of excised roots were the same whether the roots were metabolically active or inactive (table 2), a further evidence that the exchange is not governed by metabolic activity (16) but is, instead, a characteristic of the root.

If the exchange is instantaneous (3, 5, 6, 20) it should be possible to saturate the roots with any given cation by washing or rinsing them in dilute acid or salt solutions and thus eliminate the lengthy time and possible deleterious effects of electrodialysis. To check this reasoning, roots that were electrodialyzed were compared with those that had been acid-washed as a means of saturating them with H. Data in table 3 for two sets of roots are typical results of the tests. The same root sample was always used in any given set of experiments, that is, all the determinations for Series 1 (table 3) were made on one sample of excised roots, and those in Series 2 on another. Roots were carried through the determinations in the order shown, and, between successive methods used to saturate the roots with H, the H was determined by titrating the entire root system as described in MATERIALS AND METHODS. The values obtained by acid washings and titrations were lower than those obtained by subsequent electrodialysis and titration (first three determinations of Series 1). After electrodialysis and titration of the H adsorbed (the third determination of Series 1 or the first of Series 2), one 5-minute acid rinse or two or three 60-second acid rinses gave as much H upon titration of the roots as did dialysis or subsequent electrodialysis up to 5 hours. The differences noted in C.E.C. of excised roots of rough lemon in tables 1 and 3 are due to differences in size. The roots of the rooted cuttings of rough lemon in table 3 (C.E.C. of 23 me./100 g.) were larger than those obtained from the field trees (C.E.C. of 30 me./100 g.) or the seedlings (C.E.C. of 54 me./100 g.).

There may be a number of reasons why it was necessary to electrodialyze the roots first. Some material may have been adsorbed on the root surface in such

TABLE 3

Cation-exchange capacity of excised roots of rooted rough lemon cuttings either electrodialyzed or acid-washed

Determination Procedure and Order*	Cation-Exchange Capacity
	me./100 g.
Series 1	
20 minutes in acid	14.9
10 minutes in acid	19.2
Electrodialyzed 2 hours	22.4
5 minutes in acid	22.9
One 60-second acid rinse	21.8
Three 60-second acid rinses	22.8
Two 60-second acid rinses	22.2
Series 2	
Electrodialyzed 2 hours	23.0
One 60-second rinse	21.4
Two 60-second rinses	22.8
Three 60-second rinses	22.5
Three 60-second rinses	22.8
Dialyzed 5 hours	22.4
Three 60-second rinses	22.5

* Acid rinses were 150 ml. 0.002 *N* HCl.

a manner as to be only slowly removed by the acid washing, whereas through the extended period of dialysis, in addition to the continual removal of any cations released from the roots from their immediate vicinity, a complete exchange of H for all adsorbed cations may have been obtained. This material may have been either precipitates or salts that had become semi incorporated in or on the root surface during growth of the roots. A second reason could be that under the influence of dialysis the properties of cell membranes may have been changed, and although this may not have been drastic enough to cause death (5), it could have been sufficient to influence the rate of movement between the external solution and cell contents. Drake *et al.* (3) assumed release of surface-adsorbed H to be instantaneous, and further release of H to be due to cation-exchange effected by colloidal material within the root. If so, electrodialysis affects either the membranes or some other properties of the root in such a manner that this colloidal exchange material becomes more readily accessible to the H of an acid wash.

To understand better the effect of the C.E.C. of a root on adsorption of monovalent and divalent cations, the "symmetry" values of some roots to Ca and K were determined. The symmetry value is defined as the fraction, usually expressed in per cent, of the added cation that is adsorbed when the amount added is just equal to the C.E.C. of the root.

In making the symmetry determinations, the method for determining the C.E.C. of roots was modified. The H, as determined by titrating the roots in KCl solution, was defined as the "total exchangeable H." Since the stirring action during titration might have some effects on the subsequent adsorption of Ca and K by those roots in the modified method, the adsorbed H was determined in 0.5

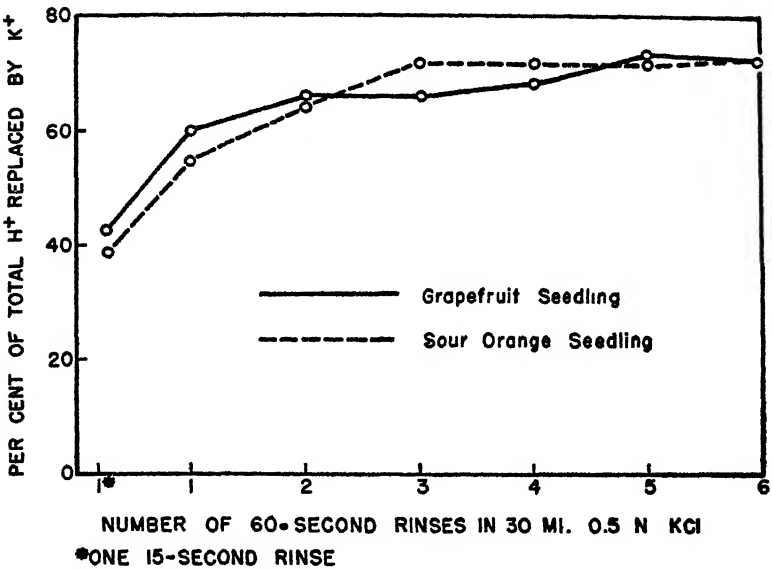

FIG. 1. RATIO OF "EASILY EXCHANGEABLE H" (THAT EXCHANGED FROM H-SATURATED ROOTS BY RINSING IN 0.5 *N* KCl) TO "TOTAL EXCHANGEABLE H" (THAT OBTAINED BY TITRATING THE H-SATURATED ROOTS DIRECTLY IN 0 5 *N* KCl FOR 5 MINUTES)

N KCl solutions in which the roots had been washed. This H was defined as the "easily exchangeable H" to differentiate it from "total exchangeable H."

Figure 1 illustrates "easily exchangeable H," for excised roots of sour orange and grapefruit seedlings. These determinations are typical of all roots examined. The values obtained for one 15-second rinse with 0.5 *N* KCl were 45 to 50 per cent of the total exchangeable H, whereas values obtained with three or four 60-second rinses were 70 to 75 per cent, which additional rinses did not increase. This is the "easily exchangeable H." It was noted that if the roots, after three or four 60-second rinses, were added to the neutralized solutions and titrations continued for 2 minutes, approximately the same amount of total base was used as when the roots were titrated directly with the KCl solution for 5 minutes.

Symmetry determinations were made as follows: Excised roots were electrodialyzed as described earlier, and the easily exchangeable H was removed by four 60-second washes in successive 35-ml. portions of 0.5 *N* KCl. The washings were combined and titrated with 0.01 *N* KOH. This gave the number of milliequivalents of H that was held by the particular sample of roots when saturated and that could be removed by KCl. To resaturate with H, the roots were passed through three 60-second washes in 0.01 *N* HCl and washed in distilled water. Excess water was removed by placing the roots between paper towels for 30 seconds, after which they were immersed in enough 0.002 *N* $CaCl_2$ or KCl to give the same number of milliequivalents of cation as the previously determined C.E.C. of the roots. Experimentation showed that the exchange was rapid, and a 2-minute rinse time was chosen. After this rinse period, the salt solution was decanted from the roots, which were then washed rapidly three times with 25

TABLE 4

Symmetry values obtained by immersing H-saturated roots separately in symmetry amounts of 0.002 N $CaCl_2$ or KCl for 120 seconds

Plant Species	Symmetry Values		
	Ca	K	Ca/K
	%	%	
Sour orange	37.5	27.5	1.36
Grapefruit	30.2	23.7	1.19
Trifoliate orange	28.8	18.3	1.56
Rough lemon	34.9	18.6	1.87
Peach	40.6	24.6	1.66
Beans	36.6	12.8	2.86
Barley	30.0	15.0	2.00

ml. distilled water. The wash waters were added to the decanted salt solution and the amount of H released by exchange with either the Ca or the K was determined by titration. Several determinations were made on the same roots by resaturating them with H before each symmetry determination.

The symmetry values obtained for 2-minute exchange periods for 0.002 *N* $CaCl_2$ or KCl are shown in table 4, with the ratio of Ca:K calculated for the results of the separate determinations for each. As an index of the ability of a root to adsorb either monovalent or divalent cations, this ratio might be better than are absolute amounts. In all cases the replacement was higher for Ca than for K. There was some indication, especially for beans and barley, that the C.E.C. might influence a shift in absorption of monovalent and divalent cations, particularly if absorption were related to the adsorption process. These values were obtained in single-salt solutions, however, and do not show the influence of one ion on the adsorption of the other. Also, the roots were saturated with H prior to the exchange determinations, and it is not unlikely that different values would have been obtained had the symmetry of Ca or K been determined against ions other than H.

Effect of C.E.C. on cation content of plants

If the density of charge on a root controls the adsorption and possibly the absorption of monovalent and divalent cations, the chemical composition of plants should show this correlation, which can be expressed by the equation:

$$\frac{\text{C.E.C.}_{1}}{\text{C.E.C.}_{2}} = \left(\frac{\text{Ca}_1}{\text{Ca}_2}\right)^2 = \frac{\text{K}_2}{\text{K}_1} \qquad (4)$$

The subscripts "1" and "2" represent different plant species. Two species are compared by comparing the ratio of their root C.E.C.'s with the square of the ratio of Ca contents and the reciprocal ratio of the K contents as given in equation 4.

There may be a number of reasons why the ratios of Ca or K contents of the leaves fail to fit the expected ratios perfectly, but discussion of these reasons will be deferred until a report on all the results has been given.

TABLE 5

Comparison of the ratios of root cation-exchange capacities of some citrus species with the square of the ratios of the Ca content and the reciprocal ratios of the K content of the leaves of Valencia orange on the various rootstocks

Plant Species Compared	$\frac{C.E.C._1}{C.E.C._2}$‡	California*		Florida†	
		$\left(\frac{Ca_1}{Ca_2}\right)^2$	$\frac{K_2}{K_1}$	$\left(\frac{Ca_1}{Ca_2}\right)^2$	$\frac{K_2}{K_1}$
rough lemon / sweet orange	1.30	0.90	1.30	1.28	1.16
rough lemon / grapefruit	1.42	0.90	1.42	1.34	1.32
rough lemon / sour orange	1.24	0.72	1.04	1.17	1.06
sweet orange / sour orange	0.92	0.81	0.79	0.92	0.92
sweet orange / grapefruit	1.11	1.00	1.09	1.04	1.14
grapefruit / sour orange	0.84	0.81	0.73	0.86	0.81

* Haas (8)—mature Valencia orange leaves from mature trees, Citrus Experiment Station, Riverside, California.

† Smith, *et al.* (17)—6-month-old leaves from 7-year-old Valencia orange trees, Orlando, Florida.

‡ Smith and Wallace (18)—cation-exchange capacity determined on seedling trees at U.C.L.A. orchard expressed as me./100 g.

Comparisons of the ratios of leaf content of Ca and K of Valencia orange trees on four different rootstocks with the respective ratio of root C.E.C. are given in table 5. The root C.E.C.'s are those determined by Smith and Wallace (18) for seedling trees in the U.C.L.A. orchard. The values obtained from data presented by Smith *et al.* (17) fit the conditions of equation 4 very well for both Ca and K content of the leaves, but values from Haas (8), though they fit well for the K content, do not fit too well for the Ca content. These differences may reflect differences in the soils of Florida and California, or perhaps the age of the trees; Smith, *et al.* (17) worked with young trees, whereas Haas (8) reported on old mature trees.

Gray *et al.* (6) have given data for the K content of Ladino clover and for either Kentucky bluegrass or bentgrass when grown in association in a given soil or in the soil with two increments of K. These data are presented in table 6 with ratios of K uptake of the various species calculated and compared with the reciprocal ratio of their root C.E.C.'s. Here, as in the data presented by Smith *et al.*

TABLE 6

*Comparison of the ratios of K contents in three plant species grown in association in soil alone and in soil plus two levels of added K, with the ratios and reciprocal ratios of their root cation-exchange capacities**

Soil Treatment	Total K Uptake per Pot (Roots Excluded)			Reciprocal Ratios of K Contents of Plants (K_2/K_1)†		
	Ladino	Bentgrass	Bluegrass	Ladino/Bentgrass	Ladino/Bluegrass	Bentgrass/Bluegrass
	mg.	*mg.*	*mg.*			
Exchangeable K..................	53.48	138.83	99.42	2.63	1.85	0.72
Exchangeable K + 120 lb. K_2O/A...	125.34	192.14	179.52	1.54	1.43	0.93
Exchangeable K + 300 lb. K_2O/A..	183.99	299.10	219.86	1.63	1.19	0.76

* Gray *et al* (6)—total uptake for three cuttings.

† Ratio of root cation-exchange capacities (me./100 g.), or $\frac{\text{C.E.C.}_1}{\text{C.E.C.}_2}$, was 2.70 for $\frac{\text{ladino}}{\text{bentgrass}}$; 2.04 for $\frac{\text{ladino}}{\text{bluegrass}}$; and 0.76 for $\frac{}{\text{bluegrass}}$.

(table 5) the fit is good for K uptake from the soil alone but not from soil to which K was added.

Data in table 7 were calculated from the results of K analysis of several legume-grass hay mixtures in the New England states given by Blaser and Brady (2). The plants compared were grown in association and thus were subjected to the same soil nutrient environment. Only in group 10 did the legume show K-deficiency symptoms. Thus, the species bromegrass and Ladino clover are compared at low K (group 10), intermediate K (group 1), and high K (group 6). The reciprocal ratio of K contents of these species correlates best with the ratio of their respective root C.E.C.'s at low K levels. The same pattern is observed with the other species, that is, bromegrass and red clover, where group 2 shows good correlation at intermediate K content, and group 7, with much higher K values, shows poor correlation. All plants grown in association with group 7 (groups 8 and 9) also show this poor correlation of reciprocal ratio of K contents to their respective ratio of root C.E.C.'s.

Some of the reasons that the ratios of Ca or K contents of two plant species do not fit the conditions of equation 4 might be: (*a*) Only a portion of the plant was analyzed and there may have been differential distribution of nutrients in different plant parts. (*b*) The levels of Ca or K, or both, in the soils were high enough for "luxury consumption" to have occurred and the influence of root C.E.C. on total monovalent and divalent uptake (9, 13, 14) thus might have been modified. (*c*) The physiological ages of the various plants or plant parts analyzed might have been very different; some plant portions might have been mature, in which case the Ca or K level, or both, would be quite different from those in the corresponding portion in an immature condition. (*d*) Errors in measurement of C.E.C. or in Ca and K contents may have occurred. (*e*) A large quantity of cations might have been present in the soil at concentrations where a Donnan equilibrium would fail. (*f*) The scion may have, as has been shown,

TABLE 7

Comparison of the reciprocal ratio of K contents of legumes and grasses, when grown in association, with the ratio of their respective root C.E.C.†*

Plant Species Compared‡	Root C.E.C.	$\frac{C.E.C._1}{C.E.C._2}$	K Contents	K_2/K_1
	me./100 g.		*per cent*	
1. bromegrass / ladino clover	24 / 43	0.56	2.54 / 1.13	0.45
2. bromegrass / red clover	24 / 48	0.50	2.54 / 1.25	0.49
3. ladino clover / red clover	43 / 48	0.90	1.13 / 1.25	1.11
4. bromegrass / alfalfa	24 / 44	0.54	2.46 / 1.46	0.60
5. ladino clover / alfalfa	43 / 44	0.98	1.50 / 1.46	0.97
6. bromegrass / ladino clover	24 / 43	0.56	2.46 / 1.50	0.61
7. bromegrass / red clover	24 / 48	0.50	3.62 / 2.75	0.76
8. alfalfa / red clover	44 / 48	0.92	2.50 / 2.75	1.10
9. bromegrass / alfalfa	24 / 44	0.54	3.62 / 2.50	0.69
10. bromegrass / ladino clover§	24 / 43	0.56	0.83 / 0.42	0.51

* Blaser and Brady (2).
† Some C.E.C. values obtained from Drake *et al.* (3) and Gray *et al.* (6).
‡ Species grown in association were groups: [1, 2, 3]; [4, 5, 6]; [7, 8, 9]; and [10].
§ Legume showed K deficiency.

exerted an influence on chemical composition of citrus trees (19). (*g*) Differential fruit yields and removal of fruit over many years may have influenced nutrient contents. And (*h*) the ratios and amounts of cations, including magnesium and sodium present in the soil, may have greatly influenced the results.

SUMMARY

The cation-exchange capacity of roots of citrus, avocado, beans, and barley was determined on an area (me./sq. m.) as well as on a weight (me./100 g. dry

weight) basis. Discussion of the value of the surface basis explains why the cation-exchange capacity of roots should probably be referred to as "density of charge."

Electrodialysis and acid-rinsing were compared as methods for saturating the roots with H prior to determining the cation-exchange capacity of roots.

The root cation-exchange characteristics were found to be of a physical nature, that is, to be the same on living and nonliving roots and as on metabolically active or inactive roots.

Symmetry values for Ca or K of excised roots of several plant species showed little correlation with Ca and K contents of the plants, although there was some influence of cation-exchange capacity of roots on the relative uptake.

As a means of evaluating the influence of root density of charge on cation uptake, the ratio of root cation-exchange capacities of two plant species grown under similar conditions was compared with the ratio of their respective Ca or K contents. For plants grown in soil of low nutrient level the ratio of Ca content of two plant species was shown to be related to the square root of the ratio of their respective root cation-exchange capacities. The ratio of K content of these same plants compared more nearly to the reciprocal ratio of their root cation-exchange capacities. Some reasons for deviations from the expected are discussed.

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A NEW METHOD FOR PREPARATION AND TREATMENT OF ORIENTED-AGGREGATE SPECIMENS OF SOIL CLAYS FOR X-RAY DIFFRACTION ANALYSIS

EARL B. KINTER AND SIDNEY DIAMOND

Physical Research Branch, Bureau of Public Roads[1]

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The use of oriented-aggregate specimens for x-ray diffraction analysis of clay minerals was first reported in 1937 by Bradley, Grim, and Clark.[2] In their relatively simple technique, wet clay was smeared on the surface of a piece of glass tubing and allowed to dry. More recently, Brown[3] developed a method that employed a centrifuge and a special tube and deposited clay from a suspension to form an oriented-aggregate on a small glass disc. Mitchell[4] has reported preparation of oriented specimens by use of pressure on small samples of powdered clay placed between the flat end of a steel rod and the flat surface of a steel plate.

These methods were specifically designed to prepare relatively small specimens for use with x-ray diffraction cameras. Somewhat larger, flat specimens, required for the now widely used, direct-recording x-ray diffraction equipment, have been prepared by air-drying clay-water suspensions on glass microscope slides. Prior to development of the improved method presented in this paper, a modification of the glass-slide technique was employed in this laboratory for specimens for a General Electric XRD-3D direct-recording x-ray diffraction apparatus. A sample of clay was dispersed in water, an aliquot of the suspension was transferred to a 1-inch by 2-inch or a 1-inch by 3-inch slide, and the clay was allowed to settle on the glass surface while the water was removed by air-drying. The slide, with the resulting flat film of clay (10 to 20 mg. of clay per square inch of surface) was then placed in the sample holder of the x-ray apparatus and its diffraction pattern obtained. Essentially this same procedure, with modification of minor details, is used in many laboratories preparing oriented-aggregate specimens.

A number of limitations and disadvantages are inherent in the glass-slide technique. Although specimens are easily prepared, several hours (usually overnight) are required for drying before patterns can be obtained. Further, the degree of particle orientation varies widely in specimens of different clays, often being little better than that of "random" specimens. This effect is partly attribut-

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able to varying degrees of flocculation and gelation in the clay suspensions and partly to inherent differences among clays. Na-bearing dispersing agents (usually sodium hexametaphosphate) are widely used to obtain adequate dispersion and prevent the flocculating effects of cations, such as H^+, Ca^{++}, and Mg^{++}, in the suspensions. Being nonvolatile, these agents necessarily remain in the dried specimens, and their crystals interfere with particle orientation and affect diffraction patterns. Ammonia, though it is volatile, cannot be safely used in many cases, since ammonium fixation may affect diffraction patterns of materials containing clay micas and vermiculites. With soil clays, it is rarely sufficient merely to prepare for each sample a single specimen and then to obtain and analyze its diffraction pattern. For the ordinary sample, it is necessary to prepare several specimens to obtain diffraction data after pretreatments such as cation replacement, heating to various temperatures, and solvation with glycerol or ethylene glycol. Conventional procedures particularly in cation replacements, involve considerable time and work, and as already noted, specimens of the same clay sample, when prepared after saturation with different cations, can vary greatly in particle orientation. Diffraction line intensities in patterns of two such specimens may thus vary so greatly, because of differences in orientation, that the effects of treatment with different cations are difficult to determine.

The physical behavior of clay films on glass slides also often presents serious difficulties. With some clays, particularly those from lateritic soils, the films do not adhere well to glass but curl away or loosen on drying, rendering the specimens unsuitable for diffraction measurements. The same difficulty occurs more often when specimens are heat-treated and frequently makes it impossible to compare diffraction line intensities before and after treatment.

A modification of Brown's centrifuge method was tried for preparation of specimens on 1-inch by 2-inch glass slides and metal plates. Although particle orientation was improved, flat, uniform films were rarely obtained with our equipment because of the tendency of the clay to pile up at the ends and edges of the specimens. Since Mitchell's pressure method is not easily adapted for the large samples required, it was not investigated.

A series of investigations which sought more suitable procedures led to development of an improved method for specimens preparation and treatment. The method consists essentially of dispersing with sodium hexametaphosphate the previously extracted clay fraction in water and depositing the clay by centrifugation as a film or "oriented-aggregate" on a flat, porous, ceramic plate. The specimen, consisting of the clay film firmly attached to the porous ceramic plate, is then washed by pulling distilled water through both the clay film and the plate by suction from a laboratory vacuum line. The specimen is then dried and a diffraction pattern recorded. Depending on the constituent clay minerals and the type of information required for completion of the x-ray diffraction analysis, one or more of several treatments are applied: for cation replacement, specimens are rapidly leached with solutions of appropriate cations and subsequently washed. Solvation with glycerol or ethylene glycol is effected by adding the polyhydric

alcohol to the original suspension or to the clay film itself after a specimen has been prepared.

MATERIALS AND APPARATUS

Clay-water suspensions

Clay-size material, previously separated from whole soil by conventional methods, is dispersed in distilled water by vigorous stirring or shaking and the use of a dispersing agent, such as sodium hexametaphosphate. Concentration of the dispersing agent is adjusted as required to prevent flocculation. Gelation is avoided by restricting clay concentration to 1 or 2 per cent.

Porous ceramic plates

Plates (fig. 1E) are prepared from white, unglazed, nonvitreous ceramic material, the biscuit form of wall tile.[5] Although their composition is not known to the authors, the tile biscuits apparently consist largely of finely ground quartz and feldspars with kaolin as binder. Having been fired once in manufacture but not vitrified or glazed, they readily absorb water to about 10 per cent of their weight. Liquids can be drawn through them by suction. Compared to laboratory filters of known average pore size, they appear to be of medium porosity. Although coherent and strong, they can easily be scored with a tungsten carbide scriber. They can be heated repeatedly to temperatures up to 700° C. (and probably higher) without damage to structure, shape, or porosity.

The dimensions of the porous plates are 1⅛ inches by 2⅛ inches by approximately ¼ inch thickness. As obtained, the tile biscuits are in two sizes, 6 inches by 6 inches by ¼ inch, and 1⅛ inches by 2$\frac{5}{16}$ inches by ¼ inch. In both sizes, they are flat on one side and slightly rounded ("cushioned") on the other. In making small plates of the size noted, the large tiles are marked on both sides, scored about $\frac{1}{16}$ inch deep on both sides with the point of a tungsten carbide scriber, and snapped apart by hand, then the excess length is removed with a bench grinder. Both forms require grinding to improve flatness of top and bottom sides. Satisfactory flatness is obtained by wet-grinding for a minute or two on a plate glass surface, using silicon carbide powder (fff grade for final treatment). After diffraction work is completed, the specimen can be stored for future reference, or the clay can be washed from the porous plate, and the plate reused. It has been observed that after repeated use of the porous plates, the rate of flow of leaching solutions is often markedly reduced. This is due to clogging of pores by the small quantities of clays not entirely removed by scrubbing. Most of these plates can be restored to their original condition by first boiling for a few minutes in a solution of sodium hexametaphosphate and then washing with water in the device shown in figure 3.

Laboratory filter plate material of medium porosity can also be used but is

[5] Obtained from Robertson Art Tile Co., Morristown, Pa., through their distributor, Mr. J. P. Sita, 2026 Georgia Ave., N.W., Washington, D. C. The authors gratefully acknowledge Mr. Sita's generous assistance in obtaining the tiles described here.

relatively expensive. With the use of tiles, the cost is only about 3 cents for one of the small plates. In experimental trials, a few plates made from laboratory clay filters (ultrafine porosity) were found to be too "tight" for reasonably rapid passage of treatment solutions, but otherwise were excellent for producing flat, smooth clay films with good particle orientation.

Centrifuge and accessories

An International Centrifuge (No. 1) equipped with a 4-place head (No. 242) and four trunnion cups (No. 373) was used. The trunnion cups were originally intended for use with 250-ml. centrifuge bottles.

Holders for porous plates and clay suspensions

A shop-made holder for a porous plate and the clay suspension is illustrated in figure 1. Essentially, it consists of an aluminum alloy base and top (A and B), two polyethylene gaskets (1/16-inch flat stock), and four brass screws. The gaskets (C) fit into flat troughs (about 1/8 inch deep) in the top and base pieces. To prepare the holder for use, the parts are assembled as in D, with the screws turned in only to the point necessary to hold the assembly together; a porous plate (E) is inserted (through the open side of the holder) between the gaskets, after which the screws are tightened. The porous plate thus forms the bottom of a rectangular well, 1 inch wide, 2 inches long, 5/8 inch deep, and of about 17-ml. capacity.

PROCEDURE

Specimen preparation

For specimen preparation, a porous plate is first wetted, either by soaking in water before assembly of the holder or by addition of sufficient water to the well of the holder after assembly, and the desired volume of clay suspension is transferred to the well. The holder is placed over the spacing ring (fig. 2 A) in the bottom of the trunnion cup (fig. 2 B), and the assemblage is then centrifuged for about 10 minutes at 2000 rpm. This deposits the clay as a uniform film on the plate and forces the water through the pores of the plate. If any water remains above the clay film after centrifugation, it can usually be removed by an additional few minutes of centrifugal treatment or be drawn out with a pipette inserted at a corner of the well. After deposition of the clay and removal of excess water, the screws are loosened about 1/8 inch, and the porous plate is removed through the open side of the holder. A prepared specimen is shown in figure 2 C. At this stage, the film is moist and soft but is firmly attached to the porous plate.

Treatment of specimens

Washing. Dispersing agents or other soluble salts can be removed from the clay by use of the device shown in figure 3 and the technique described later under *Cation replacement*.

Drying. Before a diffraction pattern is obtained, the specimen must be dried at

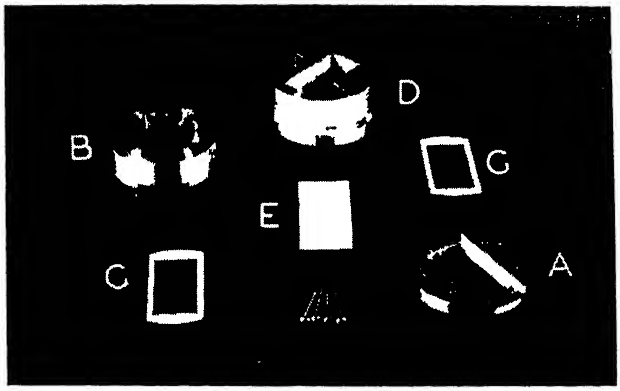

FIG 1. HOLDER FOR POROUS PLATE
A, base piece; B, top piece; C, polyethylene gaskets; D, assembled holder and plate; E, porous plate

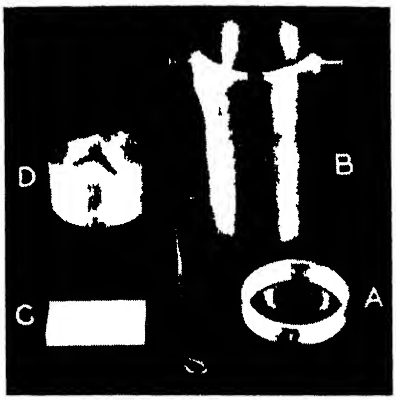

FIG. 2.

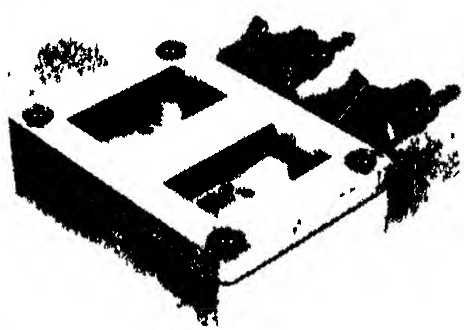

FIG. 3.

FIG. 2 SPECIMEN AND ACCESSORIES FOR PREPARATION
A, spacing ring, B, trunnion cup; C, prepared specimen, showing clay film on porous plate; D, assembled holder
FIG. 3 DEVICE FOR APPLYING SUCTION TO SPECIMENS

at least to the point where the clay film is firm to the touch; otherwise, in the specimen holder of the x-ray apparatus, the clay film will be damaged and the geometry of diffraction distorted. Most specimens may be conveniently dried in the oven at temperatures up to 70° C. In some cases an air-dried condition is desired, though, naturally drying in air is a slower process because of the water-holding capacity of the porous plate

A condition similar to that obtained by overnight air-drying can be rapidly obtained by first oven-drying the specimen, then moistening the dry clay film with wet blotting paper, a few drops of water, or a wet camel's-hair brush, and finally drying in air for a few minutes. Alternatively, the specimen can be tempered in a humidity chamber. The drying requirement applies also after any of the wet treatments subsequently described.

Heat treatment. After preliminary oven-drying, specimens are heat-treated in an electric furnace at temperatures commonly used in the study of clays by x-ray diffraction. Rapid cooling from high temperatures is to be avoided. Any glycerol or ethylene glycol in specimens should be leached out with water before heat treatment.

Solvation. Clays can be solvated with glycerol by one of the three following procedures: (*a*) addition of the polyhydric alcohol to clay-water suspensions before specimen preparation; (*b*) leaching of prepared specimens with a dilute solution of the solvating agent by use of the device shown in figure 3 and the technique described under *cation replacement*; and (*c*) application of a solution of the solvating agent directly to dried specimens.

After any of the solvation procedures, it is necessary to remove water and harden the clay film for x-raying. This can be done, without destruction of the 17.7 A. peak of montmorillonites, by brief oven-drying at 70° C., provided sufficient glycerol is present to provide a waxy clay film after drying. When there is doubt that expandable minerals in a sample will solvate if dried prior to addition of glycerol, treatment *a* or *b* must be used. With treatment *b*, specimens are removed from the centrifuge and then, before either air-drying or oven-drying, are leached with a glycerol solution.

Cation replacement. A porous plate-clay film unit is placed in one of the wells of the device shown in figure 3, vacuum is applied, and a few drops of a cation-replacement solution is added directly to the clay film. As soon as the solution is drawn through the clay, fresh solution is added. After four or five aliquots of fresh solution, the film and plate are washed with distilled water in the same manner to remove excess solution. Only small aliquots, either of solution or water, need be passed through the clay film, but the pores of the plate should finally be rinsed thoroughly with larger amounts of water. For this, water is applied from the tip of a wash bottle to fill the well-space (about 1/16-inch clearance) around the sides of the plate. Several water applications are made, and between applications a few seconds are allowed for complete drainage. At the end of the process, the specimen is ready for drying and x-raying; it can also be treated successively with a series of solutions of other cations, and diffraction patterns obtained after any treatment.

RESULTS

The new method, when applied to a wide variety of clay mineral and soil-clay samples, exhibited several distinct advantages over existing procedures. These advantages included rapid specimen preparation; better orientation in most cases; rapid and effective treatment of specimens for removal of dissolved salts, for solvations, and for cation replacement; freedom from physical destruction or alteration of oriented-aggregates upon drying and heat-treating; and facilitation of direct comparison of the diffraction effects of several treatments on a single specimen.

Starting with a clay suspension, a specimen can be prepared in the centrifuge, washed with water, and dried sufficiently for diffraction purposes in about 30 minutes. Four specimens can be centrifuged simultaneously.

TABLE 1

Diffraction intensities for air-dried soil-clay specimens on porous plates and on glass slides

Sample No.	d Value	Counts per Second Above Background		Ratio of Intensities, Plate/Slide	Mineral
		Glass slide	Porous plate		
	A.				
S-22	12.3	300	1500	5	Montmorillonite
	7.4	170	2080	12	Montmorillonite, kaolinite
S-35	14.2	810	4300	5	Montmorillonite
	7.3	185	1240	7	Montmorillonite, kaolinite
S-71	14.3	740	2200	3	Vermiculite, montmorillonite
	10.1	320	750	2	Illite
	7.2	400	1550	4	Vermiculite, montmorillonite
	6.25	30	160	5	Lepidocrocite

Sedimentation of clay by centrifugal force usually produces specimens having a high degree of particle orientation. In comparison with the glass slide technique, it has in most cases at least doubled the intensities of basal diffraction lines of the clay minerals. A comparison of diffraction intensities for specimens on porous plates and glass slides is given in table 1 for three soil clays randomly selected from a large number of samples on hand. Peak intensities of porous plate specimens ranged up to 12 times as great as those of specimens prepared on glass slides.

Deposition of clay on a porous base introduces the possibility that any resulting increase in diffraction intensity could be due not to better orientation of particles by centrifugation but to a differential fractionation in which the finer, less well crystallized clay has passed into the porous plates, leaving a higher proportion of coarser, better crystallized (and stronger diffracting) particles in the films. If such fractionation were the case, clays containing well-dispersed montmorillonite, which is extremely small in particle size, would show weaker diffraction from this mineral. Actually, however, stronger diffraction is obtained.

Further, examination of a porous plate, after a clay film has been deposited, shows that only a trace of clay can have entered the body of the plate—as attested by the sharp line of demarcation between the white plate and the brown or red soil-clay film. Occasionally, however, after centrifugation of a specimen, a trace of clay has been noted in the liquid passed through the porous plate. It has been assumed that this "passed" clay was derived from that part of the suspension immediately in contact with the plate at the beginning of centrifugation. It represents only a very small part of the total clay used. Simultaneous with the entry of this fine clay into the porous plate, a thin film of clay is laid down on the surface of the plate and serves as a fine filter upon which the remaining and larger part of the clay is deposited. Diffraction is recorded from this upper, representative part of the film.

Also of particular value in the proposed method is the ability to apply successively to a single, prepared specimen several diagnostic treatments without significantly altering orientation or other physical characteristics of the specimen. Diffraction patterns can be recorded after each treatment, and the diffraction

effects can be compared directly. This versatility applies to heat treatments, solvation, and, with special significance, to cation replacement. Aside from the advantage of direct comparison of treatment effects, considerable time and work are saved in cation replacements over that involved in conventional procedures, which require repeated treatments and washings with the use of a centrifuge. Although the clay films retard leaching and washing processes on the porous plates, most samples have not required more than 10 minutes for one exchange of cations and subsequent washing. Completeness of cation replacement has been adequate for diagnostic aid in clay mineral identification and study. For example, the effects of cationic treatments on diffraction patterns of a single specimen of a soil-clay material are shown in figure 4. The specimen (50 mg. per square inch of surface) was made from a suspension of the $<2\ \mu$ fraction of a soil derived from acid shales and sandstones. The clay consists chiefly of a vermiculite-like clay mica and kaolinite. It contains no montmorillonite or chlorite. After preparation, the specimen was successively treated with Na^+, Ca^{++}, Li^+, Mg^{++}, and K^+. After each saturation, it was washed, dried for 30 minutes at 70° C., and a pattern was recorded.

As shown in the top pattern in figure 4, with Na^+ treatment, the clay mica

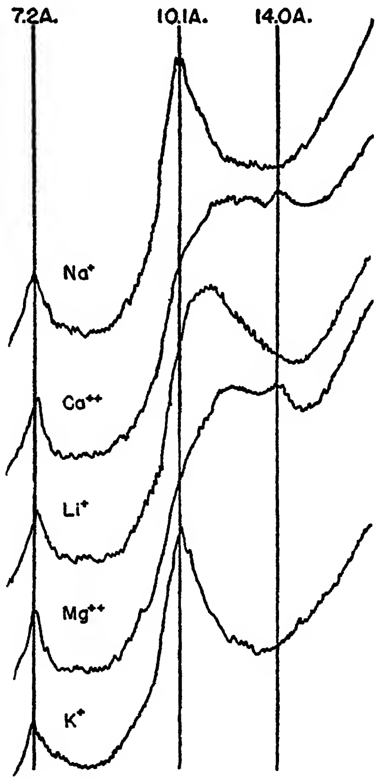

Fig. 4. X-ray Diffraction Patterns of a Single Specimen of a Soil-Clay Fraction Successively Saturated with Five Different Cations

peak remained at the usual value for illite, 10.1 A. With Ca^{++} and Mg^{++}, diffraction at 10.1 A. was diminished, with accompanying increase in the 12 to 14 A. region. Results with Li^{+} were intermediate, and upon final treatment with K^{+}, the mica layers were again collapsed to the illite spacing at 10.1 A. The kaolinite peak at 7.2 A. remained relatively unchanged throughout, at about 35 counts per second above background. This illustrates both the effectiveness of the leaching treatments for cation replacement and the constancy of particle orientation in the clay film, throughout a series of leaching and drying treatments.

If appreciable soluble salts remain in the clay after cation replacement, a considerable change in particle orientation, as indicated by the x-ray pattern, can result. This was demonstrated by leaching a specimen of a soil clay (containing kaolinite, illite, and chlorite) with *N* KCl solution as described previously, but without subsequent washing to remove excess salt. An x-ray pattern, made before the cation replacement, showed excellent orientation; another, made after cation replacement and without washing, was very similar to a "random" pattern. An examination of the treated specimen under the microscope showed the presence of small white crystals of KCl in the clay film, but after several washings with distilled water, the crystals disappeared. A third diffraction pattern made after the washing, was identical to the pattern made before the treatment. This demonstrated that crystallization of excess salts in the dry clay film interferes with particle orientation, but that the crystals can be removed by washing. More important is the fact that the leaching, washing, and drying treatments do not in themselves materially alter the original orientation of the specimen.

As described under treatment of specimens solvating agents can be applied either to suspensions before clay films are deposited on the porous plates or directly to dry clay films themselves at any stage after preparation. The latter procedure is convenient for studying the effect of any pretreatment upon solvation of constituent clays. In the present investigation, glycerol was used almost exclusively, and, by any of the procedures described, effectively solvated montmorillonites in the brief time required for specimen preparation or drying.

Film thickness of itself is not critical, but, unless clay is present in sufficient depth, intensities of diffraction peaks are reduced. Thickness of clay films is considered in terms of milligrams of clay per square inch of film surface. With glass slides, a minimum thickness of 15 mg. per square inch was used, whereas with porous plates, it was found necessary to increase this to about 30 mg. to avoid registration of diffraction emanating from quartz in the porous plates. In tests with two illite-kaolinite soil clays, maximum intensities of diffraction peaks were obtained with 100-mg. films. For cation-exchange effects, where thick films may retard leaching and washing, films of 25 to 50 mg. were satisfactory.

SUMMARY

An improved method is reported for preparation and treatment of oriented-aggregate specimens of soil clays for x-ray diffraction analysis. A thin film or aggregate of clay is deposited from a suspension by centrifugation on a flat, porous, ceramic plate. After preparation, the clay film–porous plate specimen is

given one or more of several diagnostic treatments as required for clay mineral identification and study. A diffraction pattern is recorded after each treatment. The porous plates and special devices used for preparation of specimens and application of treatments to clay films are described. Advantages over existing methods include: improved orientation of clay mineral particles, with accompanying increases in intensities of basal diffraction lines; rapid specimen preparation; freedom from loosening or curling of clay films on application of heat treatments; ease and speed of solvation, washing, and cation-exchange treatments of clay films; freedom from appreciable alteration of the original particle orientation on application of successive heat, washing, and cation-exchange treatments to a single specimen, so that diffraction patterns recorded before and after individual treatments clearly reflect the diffraction effects of each treatment.

AMPEROMETRIC TITRATION FOR CATION-EXCHANGE CAPACITY OF SOILS

R. F. HOLT

Storrs Agricultural Experiment Station[1]

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A number of investigators have determined the cation-exchange capacity of clays and soils by means of an electrometric measurement of the sorbed cation. Manuele (4), working with clays and utilizing the fact that manganese II gives a well-defined diffusion current, determined the exchange capacity polarographically. When Holtzinger *et al.* (1) extended the work of Manuele to apply to soils and compared the polarographic method with the familiar ammonium acetate and sodium acetate procedures, they obtained very good agreement between methods. Mortland and Mellor (5), utilizing a conductometric titration of barium with magnesium sulfate, showed favorable comparisons between their method and the ammonium acetate procedure on acid soils and the sodium acetate procedure on calcareous soils.

For the polarographic method, the author felt that use of a cation which would give a well-defined diffusion current at a potential less negative than that required for manganese II would eliminate the necessity of removing oxygen from the system before determining the amount of sorbed ion. Silver is a possibility, since it can be determined at the potential of a saturated calomel electrode (3) and since it has been demonstrated that the necessity of using a polarograph was obviated by the use of silver in amperometric titrations with a rotating platinum microelectrode (2), (3).

Kolthoff and Harris (2) reported a method for determining sulfur in mercaptans by means of an amperometric titration with silver in ammoniated medium using a rotating platinum microelectrode. The author[2] has utilized thiourea in ammoniacal medium as a standard solution for determining silver in complex mixtures. In this reaction, the sulfur of the thiourea is precipitated quantitatively as Ag_2S in ammoniacal medium. In the method described in this paper, thiourea is used as a standard solution to precipitate the silver held on the exchange complex. The thiourea is added in excess and the end point determined amperometrically by means of back titration with standard $AgNO_3$.

APPARATUS

The assembly used in this determination is essentially the same as that described by Kolthoff and Harris (2). It consists of a mercury-mercuric iodide, potassium iodide reference electrode with a potential −0.23 volt versus a saturated calomel electrode and a rotating platinum microelectrode. The two electrodes are shorted through a microammeter to complete the circuit. The microammeter used in this work was a Simpson Model 29 (0–20 μa. range).

[1] University of Connecticut, Storrs.

[2] Unpublished data.

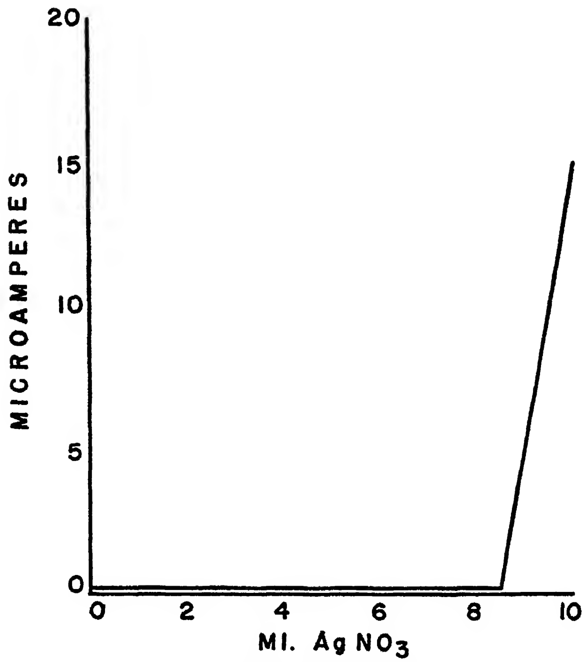

FIG. 1. TYPICAL TITRATION CURVE

PROCEDURE

Either 0.5 or 1.0 g. of soil (depending on the exchange capacity) is crushed lightly to break up the aggregates and transferred to a Gooch crucible fitted with a No. 542 Whatman filter paper. The soil is leached with 25 ml. of 0.05 *N* HNO_3, 50 ml. of 0.75 per cent silver acetate, 25 ml. of 2.5 per cent $AgNO_3$, and 50 ml. of 95 per cent ethanol, in that order, with gentle suction. Soil and filter paper are then transferred to a 250-ml. beaker and diluted to 100 ml. with distilled water, to which are then added 0.5 g. NH_4NO_3, 5 ml. of concentrated ammonia, and 50 ml. of 95 per cent ethanol. To this mixture is added 25.0 ml. of standard 0.005 *M* thiourea and the excess thiourea is back titrated with standard 0.01 *M* $AgNO_3$ to the end point as detected amperometrically by the use of a rotating platinum microelectrode. The end point is obtained graphically by taking two or three points on the ascending current portion of the titration and extrapolating back to the zero reading. A typical titration curve is shown in figure 1.

RESULTS

The exchange capacities of 15 soils from 12 states, obtained from the U. S. Department of Agriculture Soil Conservation Service at Beltsville, Maryland,[3] were determined both by the ammonium acetate method as outlined by Peech *et al.* (6) and by the proposed amperometric procedure. The results obtained by the two methods are given in table 1.

[3] The author acknowledges the assistance of Dr. V. J. Kilmer in supplying the soils.

TABLE 1

Comparison of cation-exchange capacities as determined by the ammonium acetate and the amperometric procedures

Sample and Location	pH	Cation-Exchange Capacity	
		NH_4Ac method	Amperometric method
		me./100 g.	*me./100 g.*
Leon fine sand	5.1	8.4	7.7
0–5 inches, Florida		8.3	7.9
Camden silt loam	6.8	14.1	16.4
0–5 inches, Illinois		14.2	16.7
Plainfield loamy fine sand	6.7	3.6	3.9
0–7 inches, Indiana		3.5	3.8
Haig silty clay loam	6.2	28.9	31.0
0–6 inches, Iowa		28.8	31.6
Taintor silty clay loam	5.7	34.3	37.5
0–6 inches, Iowa		33.3	37.4
Baldwin silt loam	5.8	15.6	16.8
0–7 inches, Louisiana		16.3	16.3
Holdrege silt loam	7.2	20.0	21.5
0–6 inches, Nebraska		20.5	21.4
Sharpsburg silty clay loam	6.4	28.8	30.2
0–9 inches, Nebraska		29.2	30.4
Miami silt loam	7.6	16.2	19.7
0–6 inches, Ohio		15.9	19.3
Kirkland silt loam	5.7	19.9	19.8
surface, Oklahoma		20.2	20.0
Logue silt loam	5.2	17.9	18.2
0–6 inches, Pennsylvania		18.1	18.4
Burton loam	4.3	32.2	33.8
0–6 inches, Tennessee		33.4	34.6
Amarillo loam	8.4	16.8	17.1
0–7 inches Texas		16.8	17.2
Brownfield fine sand	7.5	3.4	3.7
0–12 inches Texas		3.4	3.8
Fayette silt loam	5.9	10.3	11.5
0–7 inches, Wisconsin		10.3	11.5

The standard deviation for the amperometric procedure as calculated from the 15 duplicate determinations by the method of Youden (8) is 0.24 me./100g. The correlation coefficient calculated from the values obtained by the two methods according to Snedecor (7) is 0.9945.

DISCUSSION

As indicated in table 1 and by the standard deviation value, the amperometric method has good precision, although variations are to be expected when, as in the present case, the size of sample is small. The procedure is rapid and should be sufficiently accurate for most soil studies. Results compare well with those obtained by the ammonium acetate method.

Should chloride and readily soluble phosphate remain after the HNO_3 leaching,

use of a standard chloride solution in place of the thiourea and titration with silver in an acid 50–75 per cent acetone solution (4) at the potential of a saturated calomel electrode would be advisable. This did not prove to be necessary for the samples reported in this paper.

Occasionally the platinum electrode becomes coated with the brown Ag_2S precipitate and the electrode is rendered somewhat less sensitive. This may be remedied by gently wiping off the electrode with a cloth or the fingers. Since the soils used in this study represent a wide range of soil types, it is felt that the method will perform well under most conditions encountered.

SUMMARY

A simple and rapid method for determinating the cation-exchange capacity of soils is described. The soil is saturated with silver ions, which are then titrated amperometrically in a soil-water mixture. Results indicate good correlation between the proposed method and the familiar ammonium acetate procedure.

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SOME EFFECTS OF IRRIGATION WATER QUALITY ON SOIL CHARACTERISTICS

G. C. LEWIS AND R. L. JUVE

Idaho Agricultural Experiment Station[1]

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Water movement through the profile is an important mechanism in soil formation. During irrigation, additional waters with chemical compositions different from that of rainfall are applied to the soil. River and ground waters often acquire significant quantities of mineral salts between the time the water falls as rain and the time it is intercepted for irrigation. Under intensive irrigation these dissolved salts have certain influences on the soil.

In irrigated areas, some soil problems, such as decreased soil permeability, development of saline or alkali soils, development of chlorosis in plants, and increased requirements for specific soil amendments, are traceable to the influence of irrigation water.

In 1947 a study was initiated in Idaho to determine the influence of irrigation water on soil characteristics. This investigation had two objectives: (*a*) to determine the chemical characteristics of the irrigation waters being used throughout the state; and (*b*) to determine the effects of water of known quality on the soils under irrigation. The results of the first part of the investigation were published by Jensen *et al.* (13); this paper reports the results of the second part.

During the last 50 years the causes and effects of salinity and alkalinity in soils have been studied extensively. Causes of salinity have been reported by Magistad and Christiansen (16), Hayward and Magistad (11), and Gardner (9). Alkalinity is often a secondary effect of removal of excess soluble salts, leaving the soil colloids saturated with respect to sodium ions (1, 14, 19). When Harper and Stout (10) studied the relation of soil texture to soluble salt accumulation in irrigated soils of Oklahoma, they found that as the salt content of the water and the clay content of the soils increased, more salt was found in the soil profile. But only a few of the many publications on salinity attempt to show the relationship between salts in irrigation water and salts in soil. A considerable amount of work has been published, however, on the exchange of various adsorbed cations in the soil for cations introduced by shaking or leaching soil samples with a medium containing soluble salts, a subject closely related to this phase of the salinity problem.

Chapman and Kelley (3), Kelley, Laurence, and Chapman (15), Bushnell (2), and Hosking (12) have shown that relatively insoluble constituents, such as the carbonates and sulfates of calcium and the soil minerals themselves, have a great influence on chemical equilibriums established in soils.

[1] Idaho Agricultural Experiment Station Research Paper 398. The authors gratefully acknowledge the technical assistance of M. C. Jensen, G. O. Baker, M. A. Fosberg, and C. L. Tyler in certain aspects of this study.

Irrigation waters containing an excess of carbonates and bicarbonates may precipitate much of the calcium and magnesium and thus cause sodium to become the predominant cation in the soil solution. This theory has been postulated by Eaton (5), and corrective measures have been suggested (6). In a study of this high bicarbonate factor, Wilcox *et al.* (21) concluded that bicarbonate would have to exceed a concentration of 1.25 me. per liter of water before it could be considered important.

PLAN OF INVESTIGATION

Soil sampling sites were chosen in well-drained areas irrigated by 26 of Idaho's major water sources and a nonirrigated soil adjacent to each irrigated site was also selected.[2] At each site three samples were taken with an auger, at depths of 0–6, 6–12, 12–24, 24–36, and 36–48 inches, from the irrigated and adjacent nonirrigated soil. A composite sample was then made of the three samples from each depth. This sampling procedure was followed for 2 years, but in the third year samples were taken by major horizon separations rather than at arbitrary depths. Over the 3-year period a total of 523 composited samples were taken.

In the laboratory the following analyses were made on each sample: pH of the soil paste; pH and electrical conductivity of the saturation extract; quantitative analysis for calcium, magnesium, sodium, carbonate, bicarbonate, chloride, and sulfate on the saturation extract; total extractable calcium, magnesium, and sodium; base-exchange capacity; calcium carbonate equivalent; and gypsum content. Soluble and extractable potassium were determined on one set of samples. From these analyses exchangeable cations, exchangeable sodium percentage, soluble sodium percentage, and sodium-absorption ratio were calculated. Cation-exchange capacity was determined by Hosking's (12) method, in which cations are replaced from the soil with N ammonium acetate. The sample is first washed with ethyl alcohol and then transferred to a Kjeldahl flask. The adsorbed ammonium is determined by distillation with *N* NaOH.

Previously, by the chemical characteristics of the water sources (table 1) had been determined in a detailed 2-year investigation (13). These major water sources influence approximately 2 million acres of the 2½ million irrigated acres in Idaho. Average annual precipitation in the areas investigated is about 10 inches, approximately 15 per cent of which occurs from June to August. The principal crops in rotation on the irrigated soils are small grains, alfalfa, sugar beets, potatoes, and beans.

Most of the soil samples were taken from alfalfa or grain fields where sandy loams, loams, and silt loams at the surface became slightly heavier in texture deeper in the profile. Seventy per cent of the base-exchange capacities fall in a range from 10 to 25 me. per 100 g. of soil. Only 5 per cent of the soils had a base-exchange capacity of less than 10 me. per 100 g. of soil, and 13 per cent, higher than 31 me.

[2] The authors appreciate the cooperation of the Black Canyon Irrigation District, Emmett Irrigation District, Soil Conservation Service, and the U. S. Indian Field Service in the selection of sampling sites.

TABLE 1

Average chemical composition of irrigation waters

Source	Irrigation Period	Electrical Conductivity × 10³	Constituents E.P.M.							
			Cations				Anions			
			Ca	Mg	Na	K	CO_3	HCO_3	Cl	SO_4
Bear River at Grace	1948–49	0.72	2.47	4.06	1.57	0.34	0.96	4.96	1.40	1.38
Big Lost River at Mackay	1948	0.29	1.89	0.82	0.25	0.28	0.22	2.28	0.40	0.27
Big Wood River below Magic Dam	1948–49	0.24	1.60	0.70	0.29	0.25	0.17	2.05	0.36	0.22
Blackfoot River at Preston	1948–49	0.41	2.28	1.61	0.47	0.20	0.55	2.99	0.58	0.49
Boise River at Caldwell—Farmers Co-Op Canal	1948	0.35	1.48	0.47	1.64	0.16	0.16	2.41	0.82	0.36
Boise River at Diversion	1948–49	0.10	0.57	0.23	0.20	0.11	0.00	0.80	0.17	0.15
Boise River return flow—Notus Canal	1948–49	0.76	2.89	1.57	3.75	0.34	0.21	4.14	3.00	1.13
Bruneau River below Hot Springs	1948–49	0.20	0.74	0.28	1.05	0.18	0.13	1.39	0.37	0.30
Lemhi River at Salmon	1949	0.60	2.99	1.42	2.05	0.20	0.58	3.83	1.72	0.68
Little Wood River at Richfield	1948–49	0.31	2.04	1.02	0.26	0.18	0.33	2.52	0.46	0.22
Malad Big Spring	1948–49	0.57	2.98	2.09	0.97	0.17	0.28	3.77	0.55	1.42
Malad Warm Springs	1948	2.05	5.23	2.95	11.59	0.61	0.00	5.15	2.40	12.99
Mud Lake	1949	0.25	1.07	0.89	0.57	0.15	0.28	1.69	0.35	0.37
Owyhee Reservoir at tunnel outlet in Idaho	1948–49	0.27	1.08	0.57	1.11	0.14	0.25	1.58	0.71	0.37
Payette River at Black Canyon Dam	1948–49	0.10	0.40	0.23	0.18	0.10	0.00	0.63	0.18	0.12
Portneuf River at Topaz	1948–49	0.63	2.87	2.55	1.20	0.51	0.33	5.10	0.86	0.97
Snake River-South Fork at Heise	1948–49	0.31	2.09	0.90	0.45	0.28	0.25	2.11	0.83	0.52
Snake River at Minidoka	1948–49	0.41	2.15	1.29	0.84	0.26	0.34	2.59	0.91	0.74
Snake River at Marsing	1948–49	0.50	1.93	1.60	1.53	0.23	0.37	2.66	1.26	0.91
Weiser River at Diversion	1948–49	0.12	0.64	0.51	0.30	0.12	0.00	1.21	0.25	0.19
Raft River	1951	1.00	4.01	2.75	3.80	ND*	0.32	4.54	3.94	1.02
Teton River	1951	0.25	1.48	0.82	0.06	ND	0.00	2.38	0.12	0.12

* ND, not determined.

RESULTS AND DISCUSSION

Since irrigation waters contain certain salts in solution, the effect of the solution on soil characteristics becomes an important consideration. The purpose of this investigation was to determine the effect of the quality of irrigation water on the ions in a saturation extract, exchangeable ions, pH, and lime content of soil.

Historically, the suitability of irrigation water has been judged on the basis of its total salt content and sodium percentage. An increase in salt or sodium concentration in an irrigated soil is probably due either to poor drainage or to use of irrigation water high in salts or sodium or both. Since the soils considered in this experiment had good internal drainage, any increase in salt or sodium in the soil

TABLE 2

Salt and sodium status of irrigated and adjacent nonirrigated soils

Source	Years Irrigated (Approx.)	Irrigated Water Used per Year (Approx.)	Electrical Conductivity × 10^3 Saturation Extract		Soluble Na		Exchangeable Na	
			Irri-gated	Nonirri-gated	Irri-gated	Nonirri-gated	Irri-gated	Nonirri-gated
		acre-ft.			%	%	%	%
Bear River	50	4	0.49	1.00	20.9	26.5	1.7	1.0
	50	4	0.67	1.77	19.3	55.9	1.1	6.5
	50	4	0.70	1.73	20.1	58.3	1.1	13.0
Big Lost River	66	3	0.76	0.73	22.6	14.6	4.2	2.6
Little Wood River	40	4	0.67	2.05	19.0	62.4	1.2	11.4
Big Wood River	40	4.5	0.71	2.31	15.1	37.5	0.6	5.1
	50	4	0.56	0.40	15.0	19.6	0.5	1.1
	50	4	0.27	0.30	14.0	43.7	0.9	2.6
Blackfoot River	20	4	0.72	0.64	25.0	36.3	1.9	1.6
	20	4	0.70	0.46	11.8	9.1	0.9	0.7
	20	4	0.65	0.49	13.2	11.9	0.2	0.1
Boise River at Caldwell-Co-Op Canal	50	4	0.98	8.44	45.4	68.6	4.8	24.8
	50	3	0.74	8.85	34.7	35.1	0.9	17.1
	40	3	1.40	15.00+	33.5	56.9	4.6	28.4
Bruneau River	50	1.5	0.95	2.10	23.8	30.6	1.2	2.5
Lemhi River	88	2	0.68	4.39	31.9	72.6	2.9	15.6
Malad Big Spring	40	1.5	0.71	0.54	29.4	42.2	18.0	14.8
Malad Warm Springs.......	60	1.5	1.43	0.54	63.7	42.2	8.3	14.8
Mud Lake	20	3.5	1.22	0.73	42.0	34.3	3.8	2.8
	25	3	0.58	1.89	37.6	41.2	2.3	6.1
	20	3.5	0.60	0.58	33.0	25.0	2.8	2.5
	25	3	0.47	0.60	25.5	34.0	2.8	3.4
	20	3.5	0.43	1.06	45.8	34.5	2.9	3.2
Boise River at Diversion	30	3.5	0.64	5.10	14.9	76.7	2.5	23.8
	55	4	0.73	0.97	62.0	55.6	7.7	5.3
	55	4	0.46	5.56	26.5	77.9	1.4	20.0
Notus Canal (Boise River return flow)	29	3.5	0.75	9.82	73.3	68.8	5.3	35.2
	50	4	2.26	15.00+	47.1	70.3	5.3	19.5
Owyhee Reservoir water	10	3.5	1.01	1.71	40.1	43.4	4.4	5.0
	12	3.5	0.85	6.73	39.2	64.2	3.3	14.1
	12	3.5	3.28	6.49	63.3	59.4	15.9	15.0
Payette River	40	6	0.51	0.53	22.0	41.4	1.7	4.7
	11	3	1.84	3.68	52.0	64.4	4.9	9.0
	45	4	0.67	6.24	16.8	68.6	1.1	23.6
	45	3	0.41	1.78	27.2	58.0	0.6	9.0
Portneuf River	50	3	0.79	0.66	36.1	40.2	3.1	3.9
	50	3	1.11	0.75	61.6	30.8	11.5	2.7
	50	3	0.63	0.44	55.4	40.0	7.6	4.2

TABLE 2—*Continued*

Source	Years Irrigated (Approx.)	Irrigated Water Used per Year (Approx.)	Electrical Conductivity × 10³ Saturation Extract		Soluble Na		Exchangeable Na	
			Irri-gated	Nonirri-gated	Irri-gated	Nonirri-gated	Irri-gated	Nonirri-gated
		acre-ft.			%	%	%	%
Snake River—South Fork	55	3	0.51	0.52	16.1	11.5	2.4	1.8
	50	5	0.69	0.80	9.3	10.1	0.3	0.7
	50	5	0.69	0.63	15.6	9.1	0.5	0.1
Snake River—Minidoka	45	3	0.84	0.73	25.3	37.8	1.6	3.0
Snake River—Marsing	35	3.5	0.99	1.71	33.9	43.4	2.7	5.0
	35	3.5	1.50	8.78	34.5	50.6	2.8	13.9
	35	3.5	1.75	3.15	30.7	65.9	3.0	14.3
Snake River—Twin Falls	30	3	0.40	0.28	22.5	25.6	1.6	2.3
	17	3	0.58	0.52	27.4	11.3	2.9	0.9
	45	3	0.72	0.52	25.8	11.3	3.2	0.9
Snake River—Jerome	2	3	1.16	3.92	46.0	39.7	5.2	2.5
	35	3	0.72	3.92	22.5	39.7	5.2	2.5
Raft River	80	1.5	0.87	4.14	37.2	50.3	6.1	11.8
Teton River	35	5.5	0.56	1.87	17.7	6.3	1.1	0.7
Weiser River	30	4	0.40	1.48	17.1	30.1	0.8	2.5
	25	3.5	0.94	0.56	42.8	24.1	8.6	2.5

was attributed to the presence of these constituents in the irrigation water. The total salt and sodium contents of the irrigated and adjacent nonirrigated soils are shown in table 2. Since the complete data are too voluminous to be shown here, only averages based on the entire depth sampled are reported in table 2. Each figure represents 3 to 4 feet of the profile. Except for those soils initially very low in total salts and sodium, table 2 shows that the total salt concentration and soluble and exchangeable sodium percentages of the soils were reduced by irrigation.

Soluble salts were evenly distributed throughout the profiles of the irrigated soils. In contrast, the highest concentration of salts in the nonirrigated soils was found in the lower depths of the profile.

Although the soluble salts were evenly distributed throughout the profiles of the irrigated soils, there was a difference in the types of salts present at the different depths. Soluble calcium decreased with depth in 90 per cent of the profiles, and soluble magnesium decreased with depth in 77 per cent of the profiles. Soluble sodium, however, increased with depth in 70 per cent of the profiles. The relative concentration of salts in the saturation extract and in the irrigation water varies from year to year, both at the same site and at different sites. Figure 1 shows the distribution of various ions in the profile and the relative concentration of ions in the extract and irrigation water.

When soils are leached with salt solutions containing sodium, calcium, and magnesium, an equilibrium between the salt solution and the soil is established. Several workers have demonstrated that the equilibrium attained was dependent not only on the total cation concentration but also on the ratios of monovalent to divalent cations in the salt solutions (4, 8, 17, 18). In expressing equilibrium relationships in soils the U. S. Salinity Laboratory (20) has used the sodium-adsorption ratio (or SAR), defined as $Na/\sqrt{(Ca + Mg)/2}$ with ions expressed in miliequivalents per liter.

If equilibrium between the irrigation waters and soils has been established, there should be a correlation between the sodium-adsorption ratios of the irrigation waters and those of the saturation extract of the soil. The relationship be-

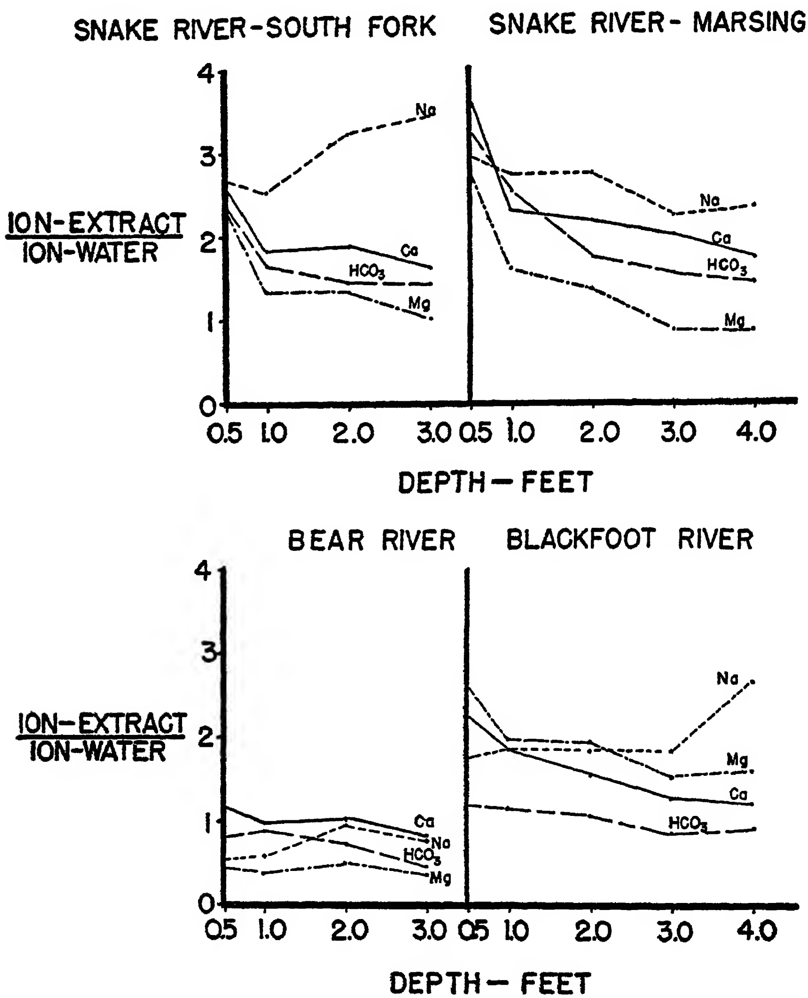

FIG. 1. DISTRIBUTION OF SOLUBLE IONS WITH DEPTH IN THE SOIL PROFILE AND THE RELATIVE CONCENTRATION OF IONS IN THE EXTRACT AND IN THE IRRIGATION WATER

tween all water sources and soils irrigated by these waters is shown by the correlation coefficients in table 3. In the top 36 inches of the soil profile there is fair correlation between the two sodium-absorption ratios.

Many of Idaho's irrigation waters are higher in carbonate plus bicarbonate

TABLE 3

Single correlation coefficients of the SAR values of irrigation water with the SAR values of the saturation extract

	Depth	Correlation Coefficient
	in.	*r*
All irrigation water sources	0–6	+0.645
	6–12	+0.731
	12–24	+0.434
	24–36	+0.893
	36–48	+0.027
Waters with no residual Na_2CO_3	0–6	+0.820
	6–12	+0.823
	12–24	+0.495
	24–36	+0.527
	36–48	+0.520

TABLE 4

Single correlation coefficients of the SAR of irrigation water with exchangeable sodium percentage (ESP) of soil

	Depth	Correlation Coefficient *r*
	in.	
SAR water *vs.* ESP..........................	0–6	+0.324
SAR water *vs.* ESP..........................	6–12	+0.409

TABLE 5

Single correlation coefficients of the SAR values of saturation extracts with exchangeable sodium percentages of soil

	Depth	Correlation Coefficient, *r*
	in.	
Irrigated soils	0–6	+0.57
	6–12	+0.43
	12–24	+0.60
	24–36	+0.93
	36–48	+0.94
Nonirrigated soils	0–6	+0.95
	6–12	+0.89
	12–24	+0.92
	24–36	+0.87
	36–48	+0.93

than in calcium plus magnesium. This high concentration of carbonate and bicarbonate upsets the equilibrium relationships of the cations, since precipitation of calcium and magnesium as carbonates leaves the excess bicarbonate, termed by Eaton (5) the "residual sodium carbonate," to react with sodium. It is difficult to assess the influence of the carbonate and bicarbonate factors on the equilibrium relationship. Exclusion of water sources containing residual sodium carbonate, however, gives a better correlation between the sodium-adsorption ratios of the irrigation water and the saturation extracts of the soils than does inclusion of such waters (table 3).

It would be useful to be able to predict the exchangeable sodium percentage of a soil from a knowledge of the sodium-adsorption ratio of the irrigation water being used on this soil. Table 4 shows a lack of correlation between the sodium-adsorption ratios of the water and the exchangeable sodium percentage of the soil, due in part to low values for both the ratios and the percentages. There is, however, a high correlation between the sodium-adsorption ratio of the saturation extract of the soil and the exchangeable sodium percentage, as shown in table 5. From a knowledge of the sodium-adsorption ratio of the saturation extract, therefore, it would be possible to predict the exchangeable sodium percentage of the soil.

Another method of showing the equilibrium relationships between irrigation waters and saturation extracts of the soil is by the relative proportions of soluble calcium, magnesium, and sodium expressed as percentages of the sum of these cations either in saturation extracts from the soils or in the irrigation water. That a close relationship exists between the percentage compositions of irrigation waters and saturation extracts of the soil can be shown by comparing the composition of saturation extracts of irrigated and nonirrigated soils with that of the appropriate irrigation water. The data indicate that soils reach a chemical equilibrium with the irrigation water applied to them. If the waters do not contain residual sodium carbonate, equilibrium in the soils has a direct relationship to the salt components of the water. If the waters do contain residual sodium carbonate, this equilibrium relationship does not necessarily occur, although here it is difficult to interpret the exact relationship. Table 6 shows the correlation

TABLE 6

Single correlation coefficients of percentage composition of ions in irrigation water and saturation extract

Comparison	Correlation Coefficient, *r*
Calcium plus magnesium (whole profile)—no residual sodium	+0.904
Calcium plus magnesium (whole profile)—residual sodium	−0.263
Calcium plus magnesium (upper 12 inches of profile)—no residual sodium	+0.871
Calcium plus magnesium (upper 12 inches of profile)—residual sodium	+0.281
Carbonate plus bicarbonate (whole profile)—no residual sodium	+0.720
Carbonate plus bicarbonate (whole profile)—residual sodium	+0.475
Sulfate (whole profile)—all irrigation waters	+0.480
Chloride (whole profile)—all irrigation waters	+0.539

coefficients which represent a comparison of the percentage composition of various ions in irrigation water with the same ions in saturation extracts of soils.

An example of equilibrium relationship between irrigation water containing no residual sodium carbonate and the soil is shown in figure 2, in respect to three sites on the Snake River. The site on the South Fork marks the section of the Snake River first used for irrigation. As the river flows down toward south-central

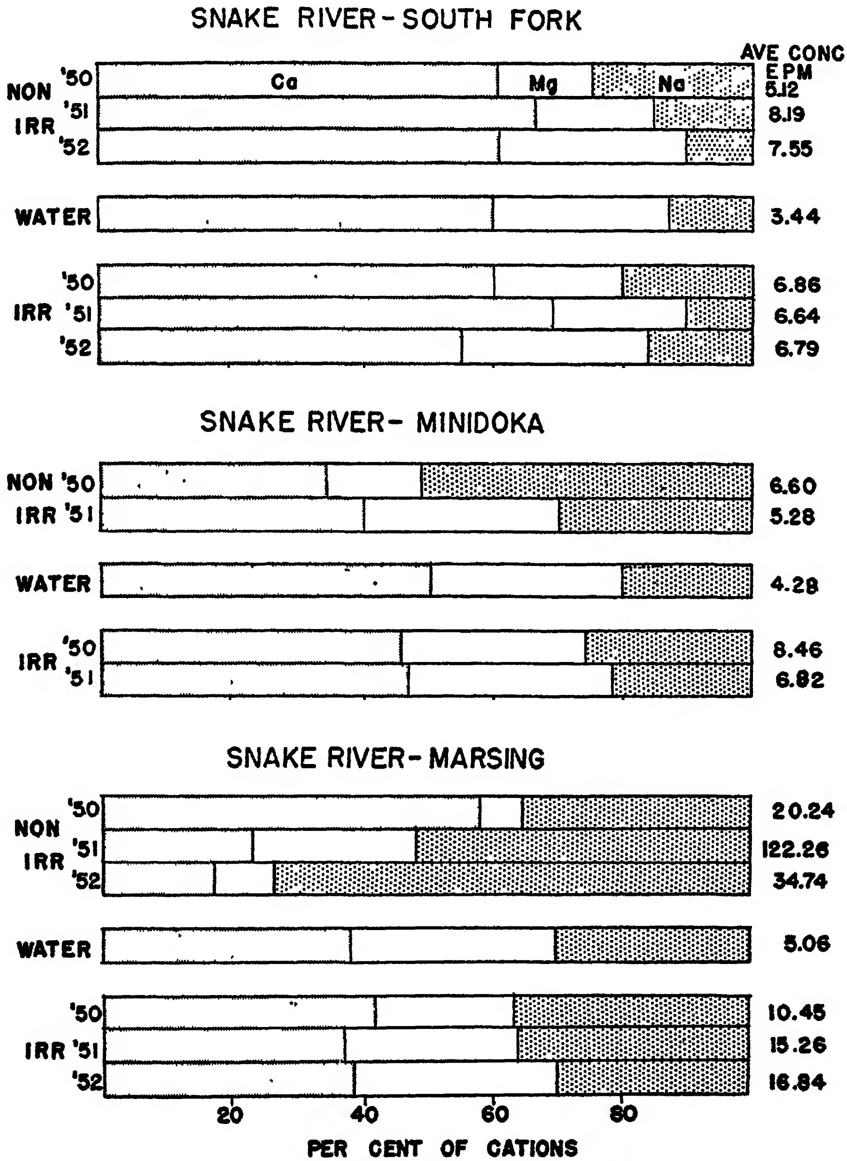

FIG. 2. EQUILIBRIUM RELATIONSHIPS BETWEEN IRRIGATION WATER AND SATURATION EXTRACTS OF SOILS AT THREE SITES ON SNAKE RIVER

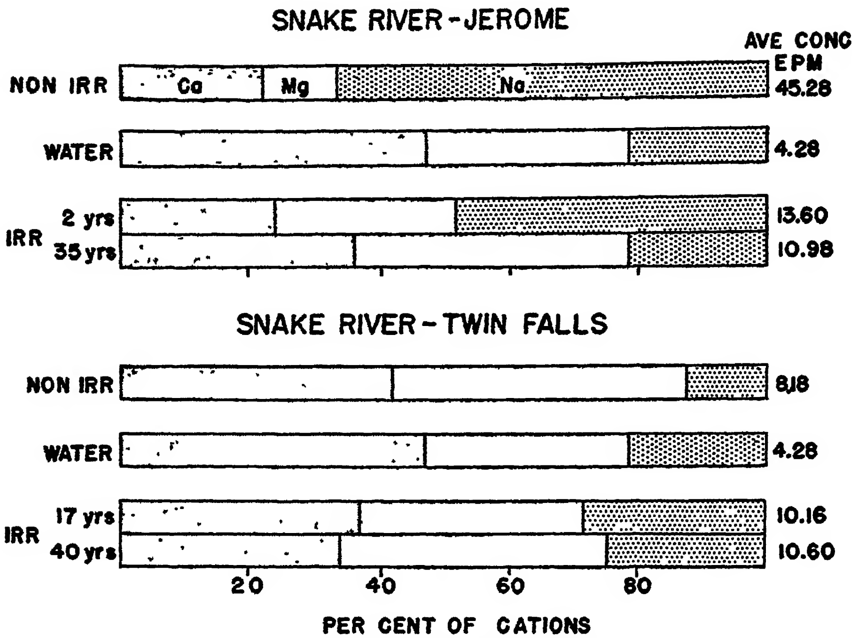

Fig. 3. Equilibrium Relationships Between Irrigation Water and Saturation Extracts of Soils at Two Sites on Snake River

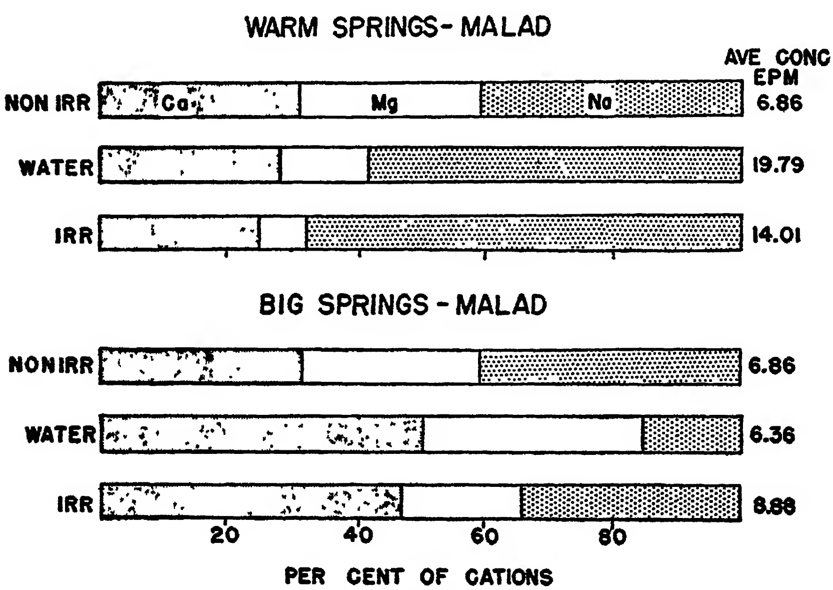

Fig. 4. Equilibrium Relationships Between Irrigation Water and Saturation Extracts of Soils of the Malad Area

Idaho both soil and irrigation water are found to contain more sodium. The relative percentages of cations in the soil, however, approach those of the water being applied. The water and soils become progressively higher in sodium as the river approaches the southwestern part of the state, and again, there is indication that the water and soils approach a chemical equilibrium.

It would be interesting to know the time required for establishment of equilibrium between the soil extract and the irrigation water. In figure 3 the Twin Falls sites, irrigated from the Snake River for 17 and 40 years, respectively, show that equilibrium has been established in 17 years. The Jerome site, irrigated for only 2 years, shows that the process of equilibrium establishment has only started, and indicates that several years will be required for equilibrium between the water and soil solution to be reached.

In the Malad area of southeastern Idaho two principal sources of irrigation water are being used. One source is the Malad Big Spring, which has a low total salt content and a low ratio of Na to Ca + Mg. The other source is the Malad

TABLE 7

Increase or decrease in calcium carbonate content of irrigated soils

Source	Gain or Loss of $CaCO_3$ in Upper 6 Inches	Gain or Loss of $CaCO_3$ in Upper 12 Inches
	%	%
Bear River	+0.08	−1.17
Big Wood River	−0.03	−0.22
Big Lost River	+2.00	+1.00
Little Wood River	+0.12	+0.06
Big Wood River	−0.03	−0.26
Big Wood River	−0.08	−0.17
Blackfoot River	+4.59	+5.36
Blackfoot River	+3.83	+4.92
Bruneau River	−0.73	−1.20
Lemhi River	+0.37	+0.26
Mud Lake	+0.92	+0.74
Mud Lake	+1.45	+4.90
Boise River	+0.04	+0.04
Notus Canal	−1.75	−1.92
Notus Canal	+3.90	+1.30
Owyhee Reservoir	−0.45	−0.35
Payette River	0.00	0.00
Portneuf River	−0.08	+0.57
Portheuf River	+0.12	+0.04
Snake River—South Fork	+0.84	+0.76
Snake River-Minidoka	+0.08	+0.08
Snake River—Twin Falls	+2.77	+7.90
Snake River—Twin Falls	+3.80	+11.96
Snake River—Jerome	+0.65	+3.47
Snake River—Marsing	+1.51	+5.13
Teton River	+0.30	+0.20
Weiser River	0.00	0.00

Warm Springs, which has a higher salt content than Malad Big Spring and a high ratio of Na to Ca + Mg. The equilibrium relationships between these two waters and the soils irrigated by them are shown in figure 4. There is a close parallelism between the percentage of individual cations found in the soils and in the water.

As a result of using irrigation water high in calcium and bicarbonate, an increase in the calcium carbonate content of the soil can be expected. Although it is significant that most sites showed an increase in calcium carbonate, the increase in lime content is not directly correlated with the calcium and bicarbonate in the irrigation water. Table 7 shows the increase or decrease in calcium carbonate in the upper 6 inches and 12 inches of soil.

CONCLUSIONS

Idaho's irrigation waters included in this study are of the quality which is effective in reducing the salt content and soluble and exchangeable sodium percentages of the soil to a level conducive to optimum plant growth.

Soluble salts were evenly distributed throughout the profiles of the irrigated soils studied. The soluble calcium content of the soil was reduced in general, with increasing depth in the profile.

There was a correlation between the sodium-adsorption ratio of the irrigation water and that of the saturation extract of the soil. This correlation improves when waters do not contain residual sodium carbonate. The amount of carbonate ion may have to be taken into consideration in evaluating equilibrium relationships between irrigation waters and soil.

There is a good correlation between the sodium-adsorption ratio of the saturation extract and the exchangeable sodium percentage of soil.

Saturation extracts from soils approach the chemical composition of irrigation waters applied to them, as is shown from the relative proportions of soluble calcium, magnesium, and sodium expressed as a percentage of the sum of these cations either in saturation extracts from soils or in irrigation waters. This equilibrium relationship is not so good when the irrigation waters contain residual sodium carbonate.

The calcium carbonate content of the soil showed an increase when irrigation waters high in calcium and bicarbonate ions (a characteristic of most of Idaho's irrigation waters) are used.

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EFFECT OF A SYNTHETIC POLYELECTROLYTE ON THE CHEMICAL, PHYSICAL, BIOLOGICAL, AND AGRONOMIC ASPECTS OF SOME PUNJAB SOILS

A. WAHHAB, A. KHABIR, M. N. AZIM, AND FAZAL UDDIN

Punjab Agricultural College, Lyallpur, West Pakistan

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The effect of alginic acid and other forms of organic matter in improving aeration, water-holding capacity, and crumb stability of soil has been shown by Quastel and Webley (26). Other workers (6, 7, 14, 15, 16, 28) have elucidated the role of polyuronides and other polysaccharides of bacterial origin in stabilizing soil structure. A number of workers (9, 11, 12, 17, 19, 21, 22) have reported the effect of various synthetic polyelectrolytes on different aspects of physical properties of soils.

Heydrick and Mowry (9), Doekel (3), and Martin *et al.* (17) obtained increased yields of various crops by using synthetic polyacrylonitriles; but Haworth and Nedler (8) observed no spectacular increases in yields after use of Krilium[1] on peas, lettuce, or turnips.

Bould and Tolhurst (2) concluded that soil conditioners had no significant effect on total dry matter of plants or on available K_2O in soil; Krilium increased the available P_2O_5 significantly, but it had no effect on P and K uptake of fertilized and unfertilized rye seedlings. MacIntire *et al.* (13) reported that the composition of crops was not significantly affected when soil conditioner was used at a rate of 0.02 per cent; heavier applications reduced Ca and Mg contents of clover and millet, increased the K content of these two crops, and reduced the K content of ryegrass. Sodium content increased with higher rates of application on limed soils. Murdock and Seay (20) found that application of the Na salt of hydrolyzed polyacrylonitrile increased the P content of wheat and the percentage recovery of fertilizer P but did not increase the yield significantly.

Fuller and Gairaud (5) observed that whereas vinyl acetate maleic acid compound stimulated biologic activity, hydrolyzed polyacrylonitrile delayed CO_2 evolution in sand.

Hedrick and Mowry (9) noted that the moisture equivalent of soil was increased without any change in the wilting point; as a result, the soil held more water available for plant growth. The rate of surface evaporation was also found to increase. Lloyd (12) observed that plants responded more favorably to Krilium if they had sufficient moisture for steady growth. Peters *et al.* (23) showed that addition of 0.1 per cent CRD-189 did not change the moisture equivalent, permanent wilting percentage, or available water in five soils ranging from sandy loam to clay.

Since some of these findings on the use of Krilium are not conclusive, response of our soils to application of this condition was of great interest.[2]

[1] Trade mark of the Monsanto Chemical Company.

[2] "Krilium" was supplied by the Monsanto Chemical Company.

TABLE 1

Mechanical composition of some Punjab soils

Per 100 g. air-dried soil

Designation	Texture	Locality	Representing	Clay (>0.002 mm.)	Silt (0.02–0.002 mm.)	Fine Sand (0.2–0.02 mm.)	Coarse Sand (2.0–0.2 mm.)	Total Carbonates
				g.	g.	g.	g.	g.
A	Sandy loam	Lyallpur	Normal fertile soil of canal colonies	14.3	26.5	56.2	3.0	0.2
B	Loamy fine sand	Jaranwala	Waterlogged and saline lands	5.5	17.6	74.0	2.9	1.0
C	Sandy loam	Montgomery	Bara lands*	15.9	35.1	44.9	Nil	5.9
D	Clay loam	Dhundi Estate	Heavy compact	30.2	39.5	30.4	Nil	10.9
E	Loam	Murree Hills	Hill tract	18.6	39.1	37.1	6.2	0.43
F	Sand	Thall	Sandy tract	4.9	6.4	71.0	17.7	0
G	Sandy loam	Lyallpur	Medium soil of canal colonies	18.6	17.7	56.6	7.1	0.3
H	Loamy sand	Lyallpur	Light sandy soil of canal colonies	7.1	10.8	51.1	31.1	0

* The clay complex of this soil is almost saturated with sodium and is impervious to water.

TABLE 2

*Chemical composition of some Punjab soils**

Per 100 g. air-dried soil

Designation	Total Water-Soluble Salts	CO_3^{--}	HCO_3^-	Cl^-	SO_4^{--}	Ca	Total N	pH (1:2; 1:2.5)
	g.	g.	g.	g.	g.	g.	g.	
A	0.22	0	0.07	0.10	0.04	0.04	0.078	7.7
B	11.87	0.01	0.13	2.79	9.12	0.51	0.151	8.6
C	1.00	0	0.12	0.31	0.54	0.02	0.048	9.1
D	0.32	0	0.09	0.10	0.11	0.03	0.107	7.7
E	0.15	0	0.09	0.02	0.03	0.04	0.202	7.3
F	0.13	0	0.08	0.01	0.02	0.03	0.032	8.0
G	0.19	0	0.10	0.05	0.04	0.03	—	—
H	0.14	0	0.08	0.02	0.04	0.04	—	—

* All anions expressed as sodium salts.

MATERIALS AND METHODS

Eight Punjab soils representing a wide range of characteristics were selected from various localities for study (tables 1 and 2).

Determination of water-soluble salts, pH, water-holding capacity, and grain analyses were made by methods described by Piper (24, pp. 36–45, 82–85, 258–266). Mechanical analysis, total carbonates, available P_2O_5 and K_2O, and total N were found by the methods of Robinson (27), Puri (25), Dyer (4),

Milne (18), and A.O.A.C. (1, p. 14) respectively. Loss of moisture was determined by weighings.

CHEMICAL STUDIES

In the first experiment, 1-pound air-dry samples of each soil from A to F were taken in sets of porcelain dishes and mixed thoroughly with 0.05 and 0.10 per cent Krilium. Treatments and checks were duplicated. Distilled water was added to bring the soils to their moisture-holding capacities. The soils were then air-dried and analyzed for total and individual water-soluble salts, pH values, total N and available P_2O_5 and K_2O (table 3).

Table 3 shows that Krilium treatment did not affect the quantity of soluble salts, pH value, or total N content. The quantities of carbonates, bicarbonates, chlorides, sulfates and calcium (not given in table 3) were also unaffected. The treatments increased available P_2O_5 in all soils; the greatest increase was in soil D, which contained the lowest available P_2O_5. Treatments also increased available K_2O in soils originally low in this nutrient; soils A and C, which were richer in available K_2O, showed a decrease due to treatments. The increases in

TABLE 3

*Effect of Krilium treatment on chemical composition of soils**

Soil Designation	Treatment	Water-Soluble Salts	Total N	Increase in Available P_2O_5 Over Control	Increase in Available K_2O Over Control	pH (1:2; 1:2.5)
		%	%	%	%	
A	Control	0.221	0.078	—	—	7.7
	0.05% Krilium	0.213	0.079	2.9	−29.3	7.7
	0.10% Krilium	0.218	0.079	4.3	−13.5	7.7
B	Control	11.872	0.150	—	—	8.6
	0.05% Krilium	11.934	0.149	6.0	22.2	8.6
	0.10% Krilium	11.843	0.150	1.1	19.1	8.5
C	Control	1.003	0.047	—	—	9.1
	0.05% Krilium	1.005	0.048	10.1	− 2.2	9.0
	0.10% Krilium	1.024	0.049	10.1	− 3.4	9.0
D	Control	0.323	0.107	—	—	7.7
	0.05% Krilium	0.347	0.107	54.4	18.4	7.8
	0.10% Krilium	0.325	0.107	19.2	1.7	7.7
E	Control	0.145	0.201	—	—	7.3
	0.05% Krilium	0.143	0.205	1.9	5.1	7.3
	0.10% Krilium	0.142	0.204	2.0	14.7	7.3
F	Control	0.126	0.031	—	—	8.1
	0.05% Krilium	0.126	0.032	5.7	28.0	7.9
	0.10% Krilium	0.128	0.032	1.4	16.5	8.0

* Data are averages of duplicates; percentages are on air-dry basis.

available P_2O_5 and K_2O were not correlated with the amount of Krilium used; they may be due to increased bacterial activity.

PHYSICAL STUDIES

Rates of percolation, water-holding capacities, and rates of moisture losses at varying intervals were also determined for these soils (table 4).

Table 4 shows that rates of percolation greatly increased in all treated soils. Sandy loams showed greatest increases; with the exception of soil E, which is a loam, coarse-textured soils, such as loamy fine sand and sand, showed less improvement. Rates of percolation increased with the increase in Krilium, but

TABLE 4

*Effect of Krilium on some physical properties of soils**

Designation	Treatment	Rate of Percolation	Moisture-Holding Capacity	Rate of Loss of Moisture, %			
				Initial moisture found	Moisture found after time intervals 22 hr	Moisture found after time intervals 46 hr	Moisture found after time intervals
		ml/hr.	%				
A	Control	5.5	39.6	35.5	22.1	4.6	—
	0.05% Krilium	25.0	41.3	40.2	25.6	6.5	—
	0.10% Krilium	30.0	42.6	40.6	27.5	7.1	—
					19.5 hr.	42 hr.	44 hr.
B	Control	17.0	45.9	41.7	30.3	21.7	20.4
	0.05% Krilium	22.1	48.8	44.0	33.2	24.2	22.7
	0.10% Krilium	28.0	48.6	47.6	37.5	27.3	25.5
					21.5 hr.	26 hr.	44 hr.
C	Control	2.3	36.1	36.0	21.4	17.6	9.1
	0.05% Krilium	9.0	40.0	38.1	23.9	20.7	12.3
	0.10% Krilium	15.2	43.5	42.0	28.0	24.1	14.6
					18.5 hr.	21.5 hr.	
D	Control	—	54.4	43.7	31.2	28.9	—
	0.05% Krilium	—	55.6	44.4	32.1	29.5	—
	0.10% Krilium	—	54.6	47.9	34.5	31.9	—
					23 hr.	27 hr.	46 hr.
E	Control	9.7	44.1	40.2	19.9	12.2	3.6
	0.05% Krilium	12.3	47.6	40.9	21.5	13.2	3.9
	0.10% Krilium	15.1	45.4	44.4	27.0	15.6	4.4
					5 hr.	24.5 hr.	
F	Control	17.0	29.6	24.4	18.9	4.4	—
	0.05% Krilium	26.9	30.8	27.0	22.0	7.1	—
	0.10% Krilium	34.0	32.5	28.0	23.1	8.4	—

* Data are averages of duplicates.

TABLE 5

Moisture losses by evaporation

Soil Designation	Treatment	Percentage Moisture Lost After Time Intervals (Difference between initial moisture and found)			Total Percentage Loss After	Percentage Moisture Lost/hr.
		22 hrs.	24 hrs.		46 hrs.	
A	Control	13.4	17.5	—	30.9	0.67
	0.05% Krilium	14.6	19.1	—	33.7	0.73
	0.10% Krilium	13.1	20.4	—	33.5	0.73
		19.5 hrs.	22 hrs.	2.5 hrs.	44 hrs.	
B	Control	11.4	8.6	1.3	21.3	0.48
	0.05% Krilium	10.8	9.0	1.5	21.3	0.48
	0.10% Krilium	10.1	10.2	1.8	22.1	0.50
		21.5 hrs.	4.5 hrs.	18 hrs.	44 hrs.	
C	Control	14.6	3.8	7.5	25.9	0.59
	0.05% Krilium	14.2	3.9	8.4	26.5	0.60
	0.10% Krilium	14.0	3.2	9.5	26.7	0.60
		18.5 hrs.	3 hrs.		21.5 hrs.	
D	Control	12.5	2.3	—	14.8	0.68
	0.05% Krilium	12.3	2.6	—	14.9	0.68
	0.10% Krilium	13.4	2.6	—	16.0	0.74
		23 hrs.	4 hrs.	19 hrs.	46 hrs.	
E	Control	20.3	7.7	8.6	36.6	0.79
	0.05% Krilium	19.4	8.3	9.3	37.0	0.80
	0.10% Krilium	17.4	11.3	11.2	39.9	0.86
		5 hrs.	19.5 hrs.		24.5 hrs.	
F	Control	5.5	14.5	—	20.0	0.81
	0.05% Krilium	5.0	14.9	—	19.9	0.81
	0.10% Krilium	4.9	14.7	—	19.6	0.80

the increase in rate was not proportional to the concentration of the soil conditioner. Krilium treatment also tended to improve the water-holding capacity of the soils; but the concentration of Krilium and the mechanical constituents of soils seem to bear no relationship to the increase in water-holding capacity.

The data in table 4 might suggest that the treatments reduced loss of moisture through evaporation; but table 5, derived from table 4, shows clearly that the treatments had little effect on rate of evaporation. Table 5 indicates percentages of moisture lost during particular intervals, total percentage moisture lost, and loss in moisture percentage per hour. Obviously, the treatments either increased moisture losses slightly or had no effect whatever. What apparently happened (table 4) was that the treatments increased the moisture-holding capacities of the soils slightly and, therefore, the initial moisture contents of the treated

soils were slightly higher than those of the controls, and these differences persisted.

STUDIES ON YIELD, QUALITY OF CROPS, AND WATER REQUIREMENTS

Useful preliminary observations were made for 0.05 and 0.10 per cent Krilium treatments alone and in combination with $(NH_4)_2SO_4$ in a pot culture experiment, with sorghum as indicator crop. The plants in Krilium-treated pots had broad deep-green leaves, well-developed root systems, and erect stout stems, whereas plants in the control pots were weak, had less firm root systems, and showed a tendency to lodge as a result of weak stems. Plants treated with $(NH_4)_2SO_4$ and 0.05 per cent Krilium gave the best yields. To mature, the untreated plants required 48 liters of water, whereas the treated plants required 72 liters.

After these preliminary observations, a second experiment was run on soils G and H, Lyallpur sandy loam and Lyallpur loamy sand, prepared as were soils A to F in the first experiment. The experiment was carried out in glazed pots holding 9 kg. of soil each. Krilium was mixed with the topsoils at rates of 0.05 and 0.10 per cent, and all the pots were wetted to their moisture-holding capacities and then sown to wheat. Just before tillering, $(NH_4)_2SO_4$ at the rate of 300 pounds N per acre was added to some pots. The plan of the experiment is indicated in table 6.

Table 6 shows that Krilium, except when used with $(NH_4)_2SO_4$, did not markedly increase yields. The increased yields with combinations of Krilium and $(NH_4)_2SO_4$ were highly significant.

Composite samples of grains from all treated and untreated pots were analyzed

TABLE 6

*Effect of Krilium alone and in combination with $(NH_4)_2SO_4$ on yield of wheat grain and straw**

Treatment	Lyallpur Sandy Loam (G)			Lyallpur Loamy Sand (H)		
	Straw increase over control	Grain increase over control	Average total dry matter including roots†	Straw increase over control	Grain increase over control	Average total dry matter including roots†
	g.	g.	g.	g.	g.	g.
Control‡	—	—	105.2	—	—	20.5
0.05% Krilium	12.5	3.5	127.1	1.1	0.2	19.3
0.10% Krilium	5.5	−3.2	124.2	1.4	0.6	20.2
$(NH_4)_2SO_4$	8.6	6.6	120.1	39.8	17.0	76.9
0.05% Krilium + $(NH_4)_2SO_4$	30.2	9.3	147.2	60.7	31.5	116.5
0.10% Krilium + $(NH_4)_2SO_4$	26.4	10.3	143.5	55.9	22.4	112.1

* Data are averages of four replicates.

† Statistical analysis showed effects of the treatments to be highly significant: Lyallpur sandy loam (soil G)—S.E. = 5.03, cd_1 = 15.49, cd_2 = 21.72. Lyallpur loamy sand (soil H)—S.E. = 3.01, cd_1 = 9.38, cd_2 = 13.23.

‡ Average yields of straw and grain from control pots for the two soils were 65.8 and 30.5 g. and 11.5 and 5.0 g. respectively.

TABLE 7

*Average quantity of water used for each treatment and transpiration ratios**

Soil	Control	0.05% Krilium	0.10 Krilium	$(NH_4)_2SO_4$	0.05% Krilium + $(NH_4)_2SO_4$	0.10% Krilium + $(NH_4)_2SO_4$
			Water used, liters			
Lyallpur sandy loam (soil G)	24.0	30.5	30.5	25.0	30.5	30.0
Lyallpur loamy sand (soil H)	11.5	12.5	12.5	21.5	26.5	26.5
			Transpiration ratios, ml. water per g. dry matter			
Soil G	228	240	274	209	208	209
Soil H	550	649	625	281	230	236

* Data are averages of four replicates.

for ash, P_2O_5, CaO, protein, and crude fiber to determine the effect of Krilium on their composition. The data showed no conclusive results, except that the fertilizer treatments increased the protein content and the 0.10 per cent Krilium treatment appeared to increase slightly the P_2O_5 and CaO contents.

Water used to mature the crop was recorded for each treatment (table 7). The data confirmed the preliminary observations made with sorghum: Krilium treatment increases the water requirements of crops, and the effect is more marked on coarse-texture soil than on fine-texture soil.

Treatment with Krilium alone increased the transpiration ratio; but $(NH_4)_2SO_4$ alone or in combination with Krilium reduced in the ratio. Differences in the transpiration ratios are very striking in the lighter soil.

TABLE 8

*Effect of Krilium alone and in combination with $(NH_4)_2SO_4$ on the yield of sorghum grain and stover**

Treatment	Lyallpur Sandy Loam (G)			Lyallpur Loamy Sand (H)		
	Stover increase over control	Grain increase over control†	Percentage increase in total dry matter	Stover increase over control	Grain increase over control†	Percentage increase in total dry matter
	g.	g.				
Control‡	—	—	—	—	—	—
0.05% Krilium	−16.4	13.0	− 2.6	2.4	0.5	4.7
0.10% Krilium	−29.6	5.4	−18.8	− 8.4	1.2	−11.7
$(NH_4)_2SO_4$	− 6.0	13.1	5.5	−21.0	2.3	−30.4
0.05% Krilium + $(NH_4)_2SO_4$	4.9	12.4	13.4	34.0	4.5	62.7
0.10% Krilium + $(NH_4)_2SO_4$	−26.6	11.7	−11.5	− 4.8	1.8	− 4.8

* Data are averages of four replicates.

† Lyallpur sandy loam—S.E. = 1.59, cd_1 = 4.95, cd_2 = 6.99. Lyallpur loamy sand—S.E. = 1.06 N.S.

‡ Average yields of stover and grain from control pots for the two soils were 116.1 and 12.6 g. and 56.4 and 5.0 g. respectively.

TABLE 9

Effect of Krilium on the decomposition of toria (Brassica compestris) *cake at different moisture levels*

Treatment	CO_2 Evolution in 4 Days		
	At 12% moisture	At 18% moisture	At 80% moisture
	mg.	*mg.*	*mg.*
Soil + distilled water	6.4	2.9	2.0
Soil + distilled water + 0.10% Krilium	7.2	5.5	5.4
Soil + distilled water + 0.25 g. toria cake	74.2	69.4	34.0
Soil + distilled water + 0.10% Krilium + 0.25 g. toria cake	105.5	99.1	51.9

This experiment was repeated with sorghum as indicator crop. The experiment was further modified by fixing the quantity of water for all treatments of each soil. For each treatment in Lyallpur loamy sand, 50 liters was used to mature the crop; in Lyallpur sandy loam, 63 liters. This modification resulted in a depression of sorghum stover (table 8).

Even under the controlled water conditions, all treatments increased grain yields, though the vegetative growth suffered from the limited water supply. Statistical analysis showed the increased yields to be highly significant in the sandy loam and nonsignificant in the loamy sand. The use of $(NH_4)_2SO_4$ with 0.05 per cent Krilium resulted in significantly higher increased yields.

In one trial, saline soil was used. The treatments and the rest of the details were similar to those in the second experiment. All pots were sown to sorghum. The control pots showed virtually no germination; but in all the Krilium-treated pots the germination was good. Growth continued for a month, then all the plants died as a result of limited drainage due to sealed drainage holes in the pots.

BIOLOGICAL STUDIES

To determine the effect of Krilium on the decomposition of organic matter, 50-g. portions of soil were taken in porcelain dishes and the treatments were arranged as in table 9. Toria (*Brassica compestris*) cake and Krilium were thoroughly mixed in dry soil, then distilled water was added and well worked into the soil. The treated samples were transferred to 500-ml. conical flasks. Decomposition of the organic matter was followed by daily measurements of the quantity of CO_2 evolved, which was absorbed in standard baryta water. Three experiments were conducted in this manner at 12, 18, and 80 per cent moisture levels.

Krilium alone increased the microbiological activity of the soil over that of the control. In presence of organic matter, Krilium markedly increased such activity. An increase in moisture level beyond 12 per cent created unfavorable conditions for microbial activity.

To determine the effect of Krilium on the bacterial population, 500-g. portions of Bari soil (C) were taken in two Kilner jars. Both the jars were brought to 12

TABLE 10

Effect of Krilium on bacterial count in Bara soil

Days	Microorganisms per g. Soil	
	Without Krilium	With Krilium
2	2,500,000	350,000
7	7,500,000	12,000,000
9	320,000	1,120,000
11	190,000	800,000

per cent moisture level, after the soil in one jar was treated with 0.10 per cent Krilium. Bacterial counts were taken at different intervals by plating on Thornton's agar. Counts are given in table 10.

In the beginning, soil bacterial population was depressed by Krilium; but after this initial setback, Krilium treatment increased microbial growth until the nutrients were gradually exhausted.

It was noted during this investigation that Krilium had no effect on azotobacter count or the rate of nitrification of $(NH_4)_2SO_4$.

DISCUSSION

Krilium treatments greatly increased the rates of percolation, which indicated an improvement in physical condition of the soil. As expected, the improvement was greater in soils containing more clay particles, a fact already noted by Moss *et al.* (19). Furthermore, Krilium may have a more pronounced effect on physically deteriorated soils. It was observed in a preliminary pot culture trial that Bara soil[3] was remarkably improved by Krilium and the improvement was reflected in significantly increased yields of Egyptian clover. Table 4 shows further that the most deteriorated Bara soil, soil C, attained greatest improvement, which is reflected in its increased percolation rates. On the other hand, soil B, from a waterlogged and saline area, is also deteriorated, though with respect to crop production only, yet it did not show much improvement. Though soil E contained more clay, there was comparatively less improvement in percolation rates. This may be due to the presence of more humus, as it is a forest soil. Since humus might already have caused physical improvement, addition of Krilium brought about only smaller changes. Thus it could be concluded that Krilium caused greater improvement in the physical conditions of deteriorated soils and of soils containing more clay. Soils already in good physical condition and those containing more organic matter were much less benefited by Krilium. Moisture-holding capacities of soils seem to be affected much as are rates of percolation.

The preliminary observations, as well as detailed experiments, showed that Krilium-treated plants required more water than did the controls. This is clear from table 7. Plants treated with $(NH_4)_2SO_4$ alone required less water than did those treated with Krilium or with both Krilium and $(NH_4)_2SO_4$. From the

[3] Soil in which soda clay has just started to form.

figures showing the amount of water needed to produce 1 g. of dry matter, however, it will be noted that addition of Krilium increased the water requirements of the crop grown. On the other hand, use of $(NH_4)_2SO_4$, whether applied alone or in combination with Krilium, reduced such requirements.

As has already been indicated, Krilium treatment produced good vegetative growth of plants with stout stems, broad leaves, and well-developed root system, though yields were adversely affected by lack of nitrogen in the later stages in comparison with treatments in which $(NH_4)_2SO_4$ was used. Krilium does not affect the rate of evaporation. There was no loss of water through drainage, because the experiments were conducted in glazed pots with sealed drainage holes. The only other means, therefore, through which increased loss of moisture could occur to increase the water requirements of the Krilium-treated pots was transpiration. As the use of Krilium resulted in better growth, therefore, loss of moisture through transpiration was much greater than in the control. The argument could be further strengthened by conclusions of Peters *et al.* (23), who showed that soil conditioners did not change moisture equivalence, permanent wilting percentage, or available moisture of soils ranging in texture from sands to clays.

Pots treated with $(NH_4)_2SO_4$ alone or in combination with Krilium also showed better growth; but still the water requirements were reduced. This may be due to the fact that during the same growth period, $(NH_4)_2SO_4$-treated plants make much better growth and thus complete their vegetative phase in a shorter period; consequently the water requirements are reduced. The delay due to $(NH_4)_2SO_4$ takes place only at the time of grain formation, when water requirements of plants are much reduced. This is true also of plants treated with combinations of $(NH_4)_2SO_4$ and Krilium. When all the pots were supplied with a limited quantity of water, however, the yields were much reduced in the treated pots; in one case nonsignificant results were obtained.

Effects of treatments on yields were highly significant. Highest yields were obtained when $(NH_4)_2SO_4$ was used with 0.05 per cent Krilium. Howard *et al.* (10), on the other hand, obtained significantly decreased yields of sugar beets with increased rates of VAMA and HPAN.

Germination of sorghum seeds in Krilium-treated saline soil was much better than in the untreated control. Possibly Krilium treatment prevented formation of a crust on the soil surface; such a crust was observable on the untreated soil.

Fuller and Gairaud (5) have suggested that Krilium treatment may have a temporary toxic effect on the soil microflora and thus cause a depression in the bacterial population in the beginning. But the temporary setback may be due more to the time taken by the microorganisms to readjust themselves to the changed soil conditions caused by Krilium than to the toxicity of Krilium.

SUMMARY AND CONCLUSIONS

The effect of Krilium on various Punjab soils was studied with respect to some physical and chemical conditions, plant growth, and microbial activity. Krilium increased the percolation rates and moisture-holding capacities but did

not change the rates of evaporation of the soils used. There was greater improvement in deteriorated soils and soils containing more clay particles. Krilium did not affect the total soluble salts, total nitrogen, and pH value of soils. But it increased the available P_2O_5 and in some soils the available K_2O. Growth in saline soils was also much improved.

Krilium treatments alone or in combination with ammonium sulfate increased significantly yields of wheat grain. Under restricted water supply, yields of sorghum were much reduced, yet on Lyallpur sandy soil significant yield increases were obtained with Krilium.

The study of the effect of Krilium on the quality of wheat grains led to no definite conclusions. There are indications, however, that use of 0.10 per cent Krilium increases the P_2O_5 and CaO content of grains.

Krilium treatments increase the water requirements of crops, whereas ammonium sulfate reduces these requirements.

Krilium treatments increase soil microbial activity, and this activity is much increased in presence of organic matter. Krilium application has a temporary depressing effect on the microbial population, though at later stages the number of bacteria is greatly increased.

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Altering Soil Properties with Chemicals. Introduced by ALAN S. MICHAELS. Industrial and Engineering Chemistry, Washington, D. C., 1955. Pp. 52. Price $1.50.

This is a bound reprint of a series of 10 papers and of a panel discussion on soil stabilization with chemicals, which appeared in the November 1955 issue of *Industrial and Engineering Chemistry* (47: 2330–2281). These papers deal with marketing the chemicals, civil engineering need for them, mixing them with soil, soil stabilization for seepage control, injection techniques, fatty quaternary ammonium salts, aluminum and iron sulfate as auxiliaries in bituminous stabilization, acrylates, soil-water relationships in stabilized soils, and heat stability of asphalt antistripping compounds. The conclusions drawn were that such chemicals have important potentialities, only a few have been made available to date, many engineering problems could probably be solved by their use, developments are slow because of lack of contact between manufacturers and soil engineers, and profit incentives are as yet poorly defined.

Annual Report of the Hirakud Research Station 1953. By R. C. HOON. Government of India Press, Calcutta, 1954. Pp. 164.

This is Research Publication 5. It deals with hydraulic works, hydrology, soil mechanics, soil chemistry, theory of flow and design of channels, and some miscellaneous matters, including some comments on soil conditioners. A dam, mostly of earth and with a maximum height of nearly 200 feet, is a major feature of the Station. Details of construction of the dam, selection of materials for it, and sediment loads are given. The chief engineer, Thirumale Iyengar, expects this Station to develop into the most important on the East Coast of India by 1956–57. Illustrations include 31 plates and at least twice that many figures.

Bibliography of the Literature on the Minor Elements and Their Relation to Plant and Animal Nutrition. Volume 4. By HERBERT S. BREWER. Chilean Nitrate Educational Bureau, Inc., New York, 1955.

The first of these volumes contained 10,000 references, the second 1300, the third, 1000. The current volume contains 1363 abstracts, representing 1747 authors and 31 elements. Author, element, botanical, and animal-nutrition indexes are provided. This series constitutes a highly important contribution to the literature, and the Bureau is entitled to the thanks of all those interested in this field of research. It is hoped the series may be continued permanently.

Bibliography of Monolingual Scientific and Technical Glossaries. By EUGEN WÜSTER. Columbia University Press, New York, 1955. Pp. 219. Price, paperbound, $2.50.

This is Volume 1 of national standards being developed by the United Nations Educational, Scientific, and Cultural Organization. The material is presented in

English and French. Any publication that lists the terms that apply to a given field of knowledge, with or without explanations other than translations, is included. The universal decimal system is employed, and publications in 27 languages are covered.

Chimie Végétale. By RENE RENAULT. Librarie de L'Enseignement Technique, Paris, 1955. Pp. 486, figs. 26. Price, paper-bound, 3.590 f.

The author of this treatise on plant chemistry, which is Volume 1 of *Chimie Agricole*, is associated with L'École Nationale des Industries Agricoles et Alimentaires and is in charge of the Ecoles Nationales d' Agriculture of France. The 28 chapters of the book deal with the elemental composition of plants; histochemistry; pigments; secretions; mineral nutrition; assimilation of carbon; nitrogen nutrition; absorption of water; synthesis of carbohydrates, proteins, and fats and their metabolism; respiration; hormones; chemistry of germination; and microbial activities. The organic chemistry of plant processes is well developed. An interesting diagram of a crystal of cellulose is shown. Reference is made to the work of nearly 500 authors, most of them European. This is an excellent review of the subject. A second volume, now in preparation, will be entitled "La Biosphere."

Classics of Biology. By AUGUST PI SUÑER. Philosophical Library, New York, 1955. Pp. 337. Price $7.50.

This is an English translation of a Spanish book by a Catalonian biologist and student of medicine, who has spent most of his time since 1939 in Venezuela. There he was charged with the task of creating the Institute of Experimental Medicine of Caracas University. He outlines the concepts of early scientists in 16 fields of research and quotes from their publications. Among these one finds such well-known names as Aristotle, Lavoisier, Liebig, Pasteur, Huxley, T. H. Morgan, Linnaeus, Lamarck, von Humboldt, Pavlov, and Haldane. The book provides highly interesting reading. The supplemental remarks of the author on each subject are illuminating.

Crop Production. By G. J. ROSE. Philosophical Library, New York, 1955. Pp. 223, figs. 113 including 9 in color. Price $10.

The author is entomologist for Micron Sprayers Limited. After discussing cultural control, he divides his subject into formulations and their choice, weed killers, insecticides, fungicides, combined formulations, rodenticides, dusting, spraying, other systems of application, equipment, and storage of chemicals. Citrus, coffee, figs, mushrooms, sisal, and tea, as well as the more common crops are considered. Under each crop, control measures of all the pests involved are summarized. The illustrations on equipment and its use are of special interest. The book covers the field exceptionally well and should be of much interest to all workers in this field of research.

Geraniums for Home and Garden. By HELEN J. KRAUSS. The Macmillan Company, New York, 1955. Pp. 194, plates 16. Price $5.

It would appear that most of the plants we know as geraniums are pelargoniums. Thus the so-called garden geranium is *Pelargonium hortorum.* But both the geranium and the pelargonium belong to the family *Geraniaceae.* In her introduction, which includes characteristics, nomenclature, and history of the genera, the authors uses the general term, geranium. Then she deals with the four main groups of pelargoniums, outlines their colors and other differences, and mentions some rare varieties. Finally, she offers suggestions on growing and propagating the plants, controlling pests, and hybridization. The plates, showing flower and leaf differences, are especially interesting and instructive. Mrs. Krauss is also the author of "Begonias for American Homes and Gardens" (Macmillan, 1947).

Indoor Plants and How to Grow Them. By A. BERTRAND. Philosophical Library, Inc., New York, 1955. Pp. 92, color plates 10, figs. 36. Price $4.75.

Originally written in French, this highly interesting and very useful book has been translated by Very Higgins into English. It has to do with soil, pots, watering, soilless cultivation, causes of failure, and description of plants. The color plates are exceptionally good. The other illustrations show a considerable variety of interesting house plants. Some constructive comments are offered about size of pots and the need to elevate them above the saucers placed under them. Miniature gardens are mentioned. Plants representing a large number of families are discussed in some detail.

Introduction to Agricultural Engineering. By H. F. MCCOLLY AND J. W. MARTIN. McGraw-Hill Book Company, Inc., New York. 1955. Pp. 553. Price $7.50.

The authors are associated with the departments of agricultural engineering of Michigan State University and the University of Idaho, respectively. The book is the thirteenth in a series of agricultural engineering publications under the consulting editorship of Quincy C. Ayres. The eight parts deal with engineering in agriculture, mechanics, farm power, machinery, electrification, processing, structures, and conservation of soil and water. Each chapter is well illustrated and contains a list of questions and some references at the end. Especially interesting features include the dates of introduction of nearly 200 items of farm machinery; a drawing for a farm shop; a graph of farm power, showing the downward trend of horses and mules and the upward trend of tractors, trucks, and various other types of powered machinery; a wiring plan for a farmstead; developments in hay drying; views of power machinery moving soil in conservation programs; and use of supplemental irrigation. This is a first-class book for beginners.

Output and Expenses of Agriculture in Some European Countries. Second Report. By Food and Agriculture Organization. Columbia University Press, New York. 1955. Pp. 230. Price, paper-bound, $0.70.

The purpose of this publication is to present statistics on "some aggregate money values for the agricultural sector of the economy." In the 15 European countries covered, the gross output in 1953 was valued at $24.9 billion and purchased materials had a value of $6.8 billion. It is noteworthy that the cost of hired labor constituted 43 per cent of the net income of agriculture in England and only 10 per cent in Belgium. Many interesting points are found under discussions of the several countries.

Potassium Symposium. The Management of the International Potash Institute, Zurich, Switzerland, 1954. Pp. 445. Price $3.50.

This book contains 21 papers presented at four sessions of the Institute under the general subjects of potassium in soils; potassium in living organisms—including animals; use of potassium in agriculture; and analytical methods. Each paper is documented and is summarized in three languages other than the original. The four languages are English, French, German, and Spanish. Special attention is directed to papers on forms of potassium in soil, by Wiklander of Sweden; importance of potassium for animals, by Leuthardt of Switzerland; effect of soil-forming factors on the potassium content of soils, by E. W. Russell of England; and determination of potassium requirements by visual symptoms and plant analysis, by Walsh of Ireland. Reference is made to the work of some 400 scientists in this field.

Prices of Agricultural Products and Fertilizers. By Food and Agriculture Organization, Columbia University Press, New York, 1955. Pp. 67. Price $0.60.

The fifth of an annual series, this volume covers the year 1954–55. Price policies and movements in Europe are first presented and are followed by prices of individual agricultural products and fertilizers, and by wages. It is of interest to note that in central Europe either fertilizer prices increased or sale value of crops decreased, or both occurred. In Finland, Norway, Austria, Greece, and Italy, price movements were favorable to farmers.

The Principles of Chemical Equilibrium. By KENNETH DENBIGH. Cambridge University Press, England, 1955. Pp. 491, figs. 47. Price $7.50.

The author is professor of chemical technology, University of Edinburgh. His purpose is to present the general theory of chemical equilibrium, including statistical development, and then to suggest its applications in chemistry and chemical engineering. The three parts are concerned with principles, reaction and phase equilibrium, and thermodynamics in relation to the existence of molecules. The student is presumed to be familiar with the general concepts of temperature and heat, but these subjects are reviewed and then developed as they should be for the final year of study in chemistry or chemical engineering. The first, second, and third laws of thermodymanics are outlined, illustrated, and applied. Sets of problems, beginning with very simple ones and becoming increasingly complicated, are appended to most of the chapters. The answers, with supplemental comments, are given in the appendix. This first-class presentation would be

especially useful for graduate students who need a thorough review of the subject.

Principles of Farm Machinery. By ROY BAINER, R. A. KEPNER, AND E. L. BARGER. John Wiley and Sons, Inc., New York, 1955. Pp. 571. Price $8.75.

This is one of the Ferguson Foundation Agricultural Engineering Series. The first two authors are associated with the University of California and the last with Massey-Harris-Ferguson, Inc. The book, intended as a text for an "upper-division course in farm machinery," deals with the more common types of field machines and with such matters as power transmission, economics, and hydraulic controls. The 22 chapters include discussions of research in farm machinery, cost analyses, materials of construction, tillage implements, earth-moving equipment, fertilizer-applying machinery, harvesting, seed cleaning, spraying, and transport. The illustrations are excellent.

The State of Food and Agriculture, 1955. By Food and Agriculture Organization of The United Nations. Columbia University Press, New York, 1955. Pp. 236. Price, paper-bound, $2.50.

Subtitled "Review of a Decade and Outlook," this publication begins with a review of the situation at the end of World War II and goes on to mobilization of resources, progress in technology, production, price movements, and the issues that lie ahead. The second part presents a 10-year review of all the important food, fiber, forest, and luxury agricultural commodities, and the outlook for them. The problems of surplus production in some countries, deficiency in others, capacity to sell or buy as the case may be, and growth in population continue to be troublesome. A percentage increase of 30 in net agricultural production during the last 10 years is reported for the world as a whole, the greatest increase being in western Europe and the least in North America.

Topsoil And Civilization. By TOM DALE AND VERNON GILL CARTER. University of Oklahoma Press, Norman. Pp. 270, plates 11. Price $3.95.

Starting with the three regional civilizations of the Nile Valley, Mesopotamia, and the Indus Valley, the authors present a rapid survey of the history of civilization in relation to the use and misuse of land resources. They point out that when ancient civilizations were overrun by conquering hordes that sacked the cities and slaughtered or enslaved the peoples, *the cities were rebuilt if the soil and other resources that built the cities remained*. Only after the land had been exhausted and eroded, did the cities, once destroyed, remain dead. The authors indicate that after soil erosion has done its work, it may be too late ever to do anything about it. They note the part played by sheep and goats, notably the latter, in the final stages of denudation of the land. They include Greece, North Africa, Italy, Western Europe, and the United States in their discussion. Finally, they point out that *conservation is largely a way of thinking and a way of living. It is as fundamental as honesty and thrift and it must be achieved in much the same way.* This is a highly interesting and worthwhile book.

The Trace-Element Content of Soils. By J. D. SWAINE. Commonwealth Agricultural Bureaux, Farnham Royal, Bucks, England, 1955. Pp. 157. Price 25/.

The author is associated with the Macaulay Institute for Soil Research, Aberdeen, Scotland. The publication is No. 48 of the Commonwealth Bureau of Soil Science, Rothamsted Experimental Station, Harpenden. It covers 43 elements individually and the rare earths as a group. Included are all the known necessary nutrient elements for animals and man, some harmful ones, and those of possible usefulness in geochemical prospecting. The author gives the location from which each sample was obtained, when this information is available; its individual analyses or the analyses reported for a group of samples; the method employed and remarks; and the reference. A bibliography of more than 600 titles is appended. A vast amount of work has gone into the compilation of this publication, which will be greatly appreciated by those concerned with research in trace elements in soils, plants, and animals.

Water. Edited by ALFRED STEFFERUD. Superintendent of Documents, Washington, D. C. Pp. 751. Price $2.

This is the 1955 Yearbook of the United States Department of Agriculture. The subject is broken up into nearly 100 units, each of which is discussed by a specialist or specialists in that particular field of study. Among the many articles are those telling what water is, what it does, how it is distributed, what can be done toward its control, and the problems presented by its deficiency and excess. Water is discussed in relation to forests, crops, ranges and pastures, yards and gardens, and wildlife. Flood prevention, flood control, irrigation, drainage, and water purification are dealt with in detail. Rain-making and reclaiming water from the sea are considered. One can find in this volume something about virtually any phase of the water question that might arise in his mind. The book is well illustrated with photographs and diagrams and constitutes a highly important contribution to the subject.

Weeds. Second Edition. By WALTER CONRAD MUENSCHER. The Macmillan Company, New York, 1955. Pp. 560, figs. 135. Price $10.

This well-known and highly useful and informative book has been revised by the addition of 71 new weeds and 12 new figures. The nomenclature has been brought up to date. The book is divided into two parts, the first having to do with dissemination, habitats, and control of weeds, and the second, and major part, dealing with specific families and species of weeds. A full page illustration pictures each of the more important species and its main parts. The control measures omit the more modern chemical procedures, merely giving a few standard references. Items of special interest are the 511,208 seeds that matured from a single plant of hedge mustard, the fact that many weed seeds pass through the digestive tracts of animals without loss of germinating capacity, and the large number of poisonous weeds to which livestock is exposed. A glossary of some 300 items and a list of about 250 references are appended. The book will continue to fill a highly important need.

The World of Bees. By GILBERT NIXON. Philosophical Library, New York, 1955. Pp. 214, figs. 16. Price $4.75.

The beginning chapter of this highly interesting book tells what a bee is, and this is followed by 22 more chapters that delve into a great variety of bee characteristics and actions. Worthy of mention are stingless bees, which somehow are just as uncomfortable to have about as are those that sting. While yet a boy, the author found bees worth watching and evidently has continued his observations ever since. The final chapter tells how to study bees. Since collecting specimens is not likely to result in any serious curtailment of numbers, the author recommends that as the starting point.

Yale Conservation Studies. Volume 4. Yale Conservation Club, Yale University, New Haven, Connecticut, 1955. Pp. 31.

This annual publication of the students' conservation club contains papers on community forests, land-use patterns, resource use in New Zealand, Midwest wildlife, water laws, conflict of interest in conservation, the herring gull, Philippine forests, and the sea lamprey. An interesting statement by Joseph Wood Krutch on standards, aims, and value judgment serves as introduction.

THE EDITORS

NOTE

The editors of SOIL SCIENCE announce that plans are being made for compilation of the third 25-volume index of the Journal, covering volumes 51 through 75 for the period January 1941 through June 1953. The proposed index, which, like the two previous cumulative indexes, is to include both author and subject listings, probably will comprise about 96 pages.

This index can be published, however, only if enough advance orders are placed to warrant the expense. In an advertisement appearing elsewhere in this issue of SOIL SCIENCE, the publishers urge immediate placement of prepublication orders with them—The Williams & Wilkins Company, Baltimore 2, Maryland.

SOIL SCIENCE

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MOLYBDENUM IN PLANT AND ANIMAL NUTRITION

It is only within the last 20 years that our knowledge of molybdenum in relation to the nutrition of plants and animals has been developed. In respect to this element, application of the findings of agricultural scientists to crop and livestock production has yielded such spectacular results that widespread interest has been aroused. This issue of SOIL SCIENCE presents a survey of the research on molybdenum in this connection. The individual lists of references compiled by the several scientists who have prepared these papers at our request have been joined into one bibliographic unit at the end of the publication. Copies of the complete issue may be obtained by writing Climax Molybdenum Company, 500 Fifth Avenue, New York City, through whose courtesy the color plates were developed.

FIRMAN E. BEAR

SYMPTOMS OF MOLYBDENUM DEFICIENCY IN PLANTS

E. J. HEWITT[1]

Long Ashton Research Station, University of Bristol, England[2]

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Symptoms of molybdenum deficiency are known to exist in more than forty higher plants. The first description of such deficiency in tomato plants by Arnon and Stout in 1939 (28) followed observations by Arnon (27) that growth of lettuce, mustard, and asparagus was improved by addition of molybdenum. Two field disorders, whiptail of cauliflower and broccoli and yellow spot of citrus, were described (67, 135) about 30 to 45 years before responsibility for the disorders was attributed to a molybdenum deficiency by Mitchell (244), Davies (80), Hewitt and Jones (165, 179), and Stewart and Leonard (324, 326).

The present report is based on culture experiments of the writer and his collaborators since 1947, including unpublished material, and on the collated records of other workers. Symptoms produced in sand culture at Long Ashton are described first and apply to plants grown with *nitrate* nitrogen unless otherwise indicated. Relative susceptibility varies greatly because of differing absolute requirements, absorptive capacity, seed reserves, and nitrogen supply.

[1] The author is indebted to Mr G H Jones, A.R.P.S., for the photographic work.

[2] Agricultural Research Council Unit of Plant Nutrition (Micronutrients).

PLANT SYMPTOMS

Chenopodiaceae

Beta vulgaris var. *crassa*. Sugar beet (fig. 1F): Cotyledons remain green and turgid for several weeks after death of other parts. Leaves are narrow and of a pale green color which becomes uniformly yellow-green. Wilting occurs at leaf tips or in petioles, which shrivel and cause leaf collapse. Margins curl upward or twist and within 4 weeks leaves scorch and wither. Young leaves blacken, and death of the growing point is followed in 6–10 weeks by death of the plants. When deficiency is less severe, expanding leaves are yellow-green as in nitrogen deficiency, with pink tinting of the margins. Leaves curl, wilt, and show pale brown scorching beginning at the leaf tip. Johnson, Pearson, and Stout (202) recorded bleaching of the old leaves before necrosis in severely deficient plants grown in a serpentine soil. Mulder (252) reported severe chlorosis and leaf cupping of plants growing in an acid ironstone soil.

Table beet (202): Symptoms are similar to those in sugar beet except for conspicuous red veins. Chard var. *cicla:* Symptoms are similar to those in sugar beet, but chard is less susceptible under soil conditions (202).

Spinacea oleracea var. *crassa*. Spinach: Johnson, Pearson, and Stout (202) found spinach the most sensitive plant tested in soil. All leaves were affected. In 8 weeks, following chlorosis and severe necrosis of successive leaves, the plants died. Mulder (252) recorded pale yellow leaves, marginal cupping, and necrosis.

Compositae

Lactuca sativa. Lettuce (fig. 1H, I). This plant is very sensitive in sand culture (180) and behaves similarly in molybdenum-deficient soils.[3] With 0.000005 ppm. Mo, leaves, including cotyledons, are pale green and later become yellow. Margins roll inward, wilt, and scorch. Leaves wither completely and plants die in 4 to 7 weeks. Less severe deficiency causes relatively narrow pale yellow-green mottled leaves with marginal necrosis and pronounced cupping. Successive leaves wither and collapse, and plants do not "heart." In water cultures, Warington (366) observed gray-blue necrotic areas at the tips of middle-aged leaves; these areas coalesced into yellow papery scorch in a ring between older and younger healthy leaves. Varietal differences occur (252, 366).

When lettuce plants are given ammonium nitrate or nitrate in sand culture, they show similar symptoms, but plants given nitrite, ammonium sulfate, or urea have not shown symptoms.

Cruciferae

The Brassica group show symptoms that differ from those in other plants and comprise the whiptail syndrome. Cauliflower is representative; variations observed in other brassicas are described separately.

Brassica oleracea var. *botrytis*. Cauliflower (fig. 2A, D, E): Cotyledons remain green and turgid for several weeks. At 0.000005 ppm. Mo, the first leaf is mottled

[3] References 202, 285a, 290, 385.

FIG. 1. Symptoms of Molybdenum Deficiency in Plants. A, leaf mottling, rolling, and tip necrosis in tomato; B, severe symptoms in 5-week-old tomato plants; C, white mottling in potato leaflets; D, bright yellow chlorosis and marginal curling of potato leaflets; E, marginal necrosis and withering of potato leaves; F, withering or blackening of old leaves and wilting of petioles of sugar beet seedlings with large green cotyledons; G, leaf "scald" and withering in dwarf bean in foreground grown for third generation without molybdenum (leaves in background from normal seed); H, moderate symptoms of cupping, chlorosis, and

FIG. 2. SYMPTOMS OF MOLYBDENUM DEFICIENCY IN CRUCIFERAE. A, whiptail leaves in cauliflower given ammonium sulfate—note initial chlorotic breakdown in leaf at left; B, severe primary symptoms in Savoy cabbage—note green cotyledon and oldest leaf: C.

10 to 14 days after seeds are sown. Bright yellow mottling or bleaching between pale green veins extends over the whole lamina in successive diminutive leaves often cupped at the margins. Marginal areas appear water-soaked, membranous, and partly translucent. Wilting follows in a few hours, and the marginal areas wither and curl inward progressively until the leaf drops. Many petioles wilt before margins collapse; then leaves wither but remain attached for several days. Symptoms develop quickly in 2 to 4 days in successive leaves. Oldest leaves are sometimes less affected than adjacent leaves, but symptoms recur unchanged in youngest leaves, and plants die. These symptoms are designated primary symptoms (6, 7, 179).

Plants given 0.00005 ppm. Mo are initially green and show little or no mottling. Such plants, or those that have made temporary recovery, later show distinct secondary symptoms of whiptail, which appear about 7 to 10 weeks after seeds are sown. They involve young leaves and rarely develop in plants showing severe primary symptoms. Small yellow-green or ivory chlorotic translucent areas develop near the base of a young leaf when about 6 to 15 cm. long. There are usually three to six such areas in a single vertical row between major veins close to one or both sides of the midrib. These areas rapidly become necrotic and perforate. As the leaf expands, they produce irregular stellate holes. This stage is usually confined to one or two leaves. In subsequent leaves the breakdown occurs increasingly in the marginal regions. This causes cessation of lamina growth but not of leaf elongation. These leaves are often twisted and elongate with varying amounts of narrow, irregular lamina, except for a limited area of entire but often distorted lamina at the apex. The lamina is often corrugated, irregularly cupped, relatively thick, turgid, and abnormally dark or blue-green. In young leaves up to 3 cm. long the margins may show water-soaking and brown necrosis when the lamina is only a few millimeters wide. If these leaves elongate they are almost or totally devoid of lamina. Such leaves may fail to elongate, but they exude a clear brown fluid, become gelatinous, and finally die in 24 hours, leaving a dried brown pyramid of dead tissue surrounding the terminal bud. Death of the growing point usually occurs at this stage, but leaf primordia may develop into rounded stumps. The growing point of the leaf may die, and these leaves cease to elongate becoming stunted and brown at the apex, with distortion of the lamina behind. The old leaves of these plants remain normal except that many are thick, turgid, and dark green. Plants showing moderate primary symptoms may develop secondary symptoms directly at the margins of young leaves. Death of rudimentary leaves and of the growing point may follow rapidly. The extent, timing, and relative predominance of the various stages described vary and result in a variety of final forms that comprise the general condition called "whiptail." At 0.0005 ppm. Mo, mild leaf malformations occur, and leaf angles are wide. At 0.00005 to 0.0005 ppm. Mo, the flower curds are irregular with leafy bracts dividing the curd into several areas. Pedicels wilt after elongation, and flowers die without setting seed, or seeds remain green or pale brown and shrivel before maturing.

Cells in the initially chlorotic areas readily part when sectioned. The middle

lamella shows apparently decreasing staining capacity with hematoxylin or safranin toward the center of affected areas and is ultimately invisible.

Cauliflower and broccoli growing in molybdenum-deficient soils show the whiptail symptoms just described, with many variations.[4] Basal lateral malformed shoots may arise in whiptail plants (244, 281). Plants showing whiptail in the field are usually dark green, but mottling and chlorosis sometimes occur.[5] This mottling often disappears before whiptail symptoms appear (281) or when they become pronounced (363). Mulder (252) observed that cotyledons remain green on mottled plants in the field. Varieties differ materially in susceptibility (67, 244, 363).

Sand culture plants given ammonium nitrate show primary symptoms, but mottling is less pronounced. Foliage has a gray tint, and veins are darker green. Leaf cupping, wilting, scorching, and interveinal withering are still severe. Whiptail symptoms develop as described earlier. Plants given ammonium sulfate, nitrite, urea, or glutamic acid all show typical whiptail symptoms but do not show primary symptoms (7). Without exception, symptoms begin with the translucent chlorotic interveinal areas described earlier. In presence of non-nitrate treatments, in contrast with nitrate or with presence of molybdenum, cotyledons soon fade.

B. oleracea var. *gemmifera*. Brussels sprouts: The first true leaf may remain green and turgid like the cotyledons for a few weeks after symptoms progress in younger leaves. Foliage is initially gray-green, and mottling is often mainly around leaf margins. Leaf cupping is particularly marked. Plants die in 10 to 14 weeks when 6 to 18 cm. high. Brussels sprouts show less tendency to recover than do cauliflower, swede, or Savoy cabbage.

Plants growing in molybdenum-deficient soils tend to be gray-green. In outline the markedly cupped leaves tend to be somewhat rectangular rather than oval and they may be mottled. Young leaves may be reduced to twisted narrow outgrowths lacking normal lamina (285a).

B. oleracea var. *capitata*. Summer cabbage: Acute mottling, bleaching, and scorching may occur in older leaves (202) of plants growing in molybdenum-deficient soils, followed by malformation of young leaves and poor hearting (252). The malformed leaves are generally pale, small, and narrow, with irregular margins and some cupping (285a).

B. oleracea var. *bullata-subauda*. Savoy cabbage (fig. 2B): Leaf cupping and membranous water-soaked margins are pronounced. Veins may be purple tinted, and the general color is olive-green. Leaf angles are wide, which prevents "hearting," and lateral buds grow out. When secondary symptoms occur, young leaves may become brown, necrotic, and malformed on expansion at the margins. Rudimentary leaves turn brown and shrivel, and death of the growing point follows brown exudation. In acid soils (285a) young leaves may be abnormally narrow, twisted, and densely clustered. Old leaves are cupped and scorched, and hearting is prevented.

[4] References 67, 202, 244, 252, 281, 285a, 363, 386.

[5] References 202, 252, 285a, 363, 386.

B. oleracea var. *ramosa*. Marrowstem kale: Seedlings are pale gray-green, and oldest leaves may be less chlorotic than middle leaves. Marginal cupping, wilting, inrolling, and pale brown scorching follow. Irregular interveinal scorching of young leaves and death of the growing point may follow temporary recovery. Similar symptoms appear with ammonium nitrate. In acid soils pronounced mottling and marginal cupping occur (285a). These symptoms, however, are often due to manganese toxicity (166).

B. oleracea var. *acephala*. "Thousand head" or "hungry gap" kale: Seedlings are pale green with bright yellow mottling between veins except in oldest leaves. Leaf cupping is virtually absent, but wilting, scorching, and withering progress as in cauliflower. After temporary recovery young leaves become brown at margins, and the midrib elongates with little or no lamina. The leaf tip finally turns brown and dies. Leaf mottling and necrosis may occur in acid soils (202).

B. napus. Rape: Initial symptoms resemble "thousand head" kale. Plants appear rosetted but survive for many weeks in the severely scorched conditions. Similar symptoms appear with ammonium nitrate.

Plant (285a) observed no symptoms in rape growing in an acid soil adjacent to cauliflower acutely affected by whiptail. Rape in acid soils may show mottling (252) or pale leaves with malformation analogous to whiptail (226).

B. rapa. Swede (fig. 2C): At 0.000005 ppm. Mo, leaves are dull, pale green with marginal cupping 17 days from sowing. Margins become gray, curl inwards, wilt and scorch in a few hours, and later wither completely. Plants may die in 4 to 8 weeks. Plants grown at 0.00001 to 0.00005 ppm. Mo, or those that have made temporary recovery later show brown margins of young leaves. These expand with severe cupping, marginal distortion, and reduced lamina. Later leaves become brown and die at the leaf tip; they produce a stunted petiole lacking any lamina or sometimes elongate with narrow irregular lamina characteristic of whiptail. Waring (364) recorded mottling and young leaf-edge burn in swede-turnip in the field.

Turnip: Severe chlorosis, bleaching, and death of older leaves occurred in turnips grown in molybdenum-deficient serpentine soil (202) where turnip was as sensitive as lettuce and sugar beet and far more so than broccoli or kale.

Raphanus sativus. Radish (fig. 2F): Plants grown with approximately 0.00001 ppm. Mo are pale green with bright yellow interveinal mottling of the older leaves 3 weeks after sowing. Cotyledons are large and green for 5 to 6 weeks. Leaf margins are markedly cupped. Fluid exudes on the leaf surface and water-soaked areas appear. Margins wilt, inroll, and wither. Leaves wither completely except for petioles. Secondary symptoms have not been observed, and symptoms progress from oldest to youngest leaves until plants die. Flowers die before opening. Leaf cupping, chlorosis, and marginal necrosis occur in radish plants in molybdenum-deficient soils (202, 252), while cotyledons appear to remain green (252).

Sinapis alba. White mustard: Plants show paling of the lower leaves followed by interveinal yellow-green mottling. Margins bleach, wither, and curl inward, usually from the leaf tip. Old leaves may be less affected than midstem leaves,

which become completely withered. Mustard was more sensitive than radish in serpentine soil (202).

Cucurbitaceae

Cucumis melo. Rock melon: Wilson (387) described stunted plants with pale green foliage showing interveinal yellow-green chlorosis and a narrow brown marginal scorch followed by severe marginal withering.

Cucurbita pepo var. *verrucosa*. Squash: Squash plants growing in molybdenum-deficient soil were chlorotic with some necrosis (202) and were comparable to broccoli in sensitivity.

Gramineae

Avena sativa. Oat var. *Red Algerian:* Plants are erect with pale green leaves. Slight interveinal chlorosis is accompanied by gray interveinal lesions, which later become brown, or orange-red flecks with leaf-tip scorching. Growth and grain formation are decreased. Piper (273) grew Algerian oat in water culture. Necrotic lesions first appeared about midway along upper leaves; they extended across the width of the leaf and caused collapse at the midpoint. Necrotic areas dried out with a red-brown scorch. Grain production was markedly decreased. "Blue chaff" disease of Algerian oat in Tasmania (142) where glumes are blue-green may be caused by molybdenum deficiency.

Hordeum vulgare. Barley: Growth is drooping, and stems are limp. Foliage is dull pale green. Leaf tips and margins develop gray interveinal necrotic areas and rapidly scorch. Middle-aged leaves are most sensitive. Leaf-tip scorch extends irregularly, leaving isolated areas of initially unaffected tissue. Youngest leaves remain rolled and chlorotic with a constriction near the apex as in copper deficiency. Stems collapse after death of youngest leaves before emergence. Flowering is decreased and grain formation suppressed. By use of water culture, Mulder (247) observed chlorotic striations and tip necrosis in the younger leaves. Grain production was poor, and late tillers developed.

Triticum aestivum. Wheat: Wheat grown in acid soil from molybdenum-depleted seed (252) appeared chlorotic. Many glumes were empty, ripening was delayed, and kernels were shriveled as in copper deficiency.

Secale cereale. Rye: Plants are limp and drooping with pale yellow or gray-green leaves that have white tips and irregular longitudinal bleached areas.

Dactylis glomerata. Cocksfoot; *Lollium perenne*. Perennial rye grass; and *Holcus lanatus*. Yorkshire fog: These grasses show pale yellow-green foliage, as in nitrogen deficiency, and extensive bleached areas followed by withering.

Phleum pratense. timothy: Marked chlorosis appeared in plants grown in molybdenum-deficient soil (202).

Leguminosae: I. Small-seeded species

Trifolium pratense and *T. hybridum*. Red clover and alsike: Foliage is pale or dull gray-green. Margins of older leaves fade, curl inward, become limp, and develop red-brown, or pale brown scorch with interveinal necrosis. Petioles

wilt, and leaflets wither. Warington (367) observed also a blue tint prior to scorching in red clover.

T. subterraneum. Subterranean clover: Molybdenum deficiency in the field causes symptoms of nitrogen deficiency due to depressed nitrogen fixation in the root nodules. Root nodules are smaller and more numerous (15). Nitrogen-deficiency symptoms and increased nodulation occur in molybdenum-deficient red and white clovers (252, 367). Clovers given nitrate in the field, because of their low requirements under these conditions (15, 202, 252), show no symptoms.

Medicaga sativa. Lucerne or alfalfa: Foliage is dull pale green. Leaf margins appear gray, limp, and curled. Interveinal leaf-tip necrosis is followed by rapid bleaching to white scorch. Leaves wither completely, and petioles wilt and collapse. Symptoms develop mainly in "midstem" or in younger leaves. Evans, Purvis, and Bear (117) recorded similar symptoms in culture experiments. Mulder (252) found more numerous, slender yellow nodules instead of larger red ones in deficient field plants.

Leguminosae: II. Large-seeded species

Water and sand culture experiments (184, 237) show that the molybdenum content of the seed determines the appearance of symptoms in this group. Peas and beans may hold sufficient molybdenum for two generations of almost normal growth without molybdenum, but severe symptoms may develop in the third generation. Such deficient seed, however, produces normal full-yielding plants when grown in a complete nutrient solution.

Pisum sativum. Pea: Plants grown from seed raised through two generations of molybdenum deficiency are dwarfed and pale in 15 days. Old leaves wilt suddenly, curl up, scorch at margins, and finally wither completely. Plants wither or may produce a weak basal shoot. Flowering is totally suppressed.

Plants grown from seed depleted during only one generation are larger, and pale green, and do not usually die. Lower leaves are affected, as described, in 5 to 8 weeks, and younger leaves continue to be produced. A few flowers produce viable seeds. Meagher, Johnson, and Stout (237) observed interveinal collapse while the tissues were still green. There was no apparent difference in initial growth; during the day symptoms appeared suddenly without preliminary mottling.

Phaseolus vulgaris. Dwarf french bean (fig. 1G): With three generations under deficiency conditions, plants have large pale green leaves that become mottled interveinally and rapidly develop large irregular interveinal pale brown scorched areas. Leaf margins wilt, and leaves wither and fall. Prophylls are chlorotic, become scorched or necrotic, and wither. Flowering is suppressed. With two previous generations of deficiency or one generation, symptoms are less acute and take longer to appear. They may comprise only slight mottling and occasional necrotic patches. Some flowers are produced and set seed.

Meagher, Johnson, and Stout (237) obtained similar results from deficient seed. Mottling, followed by tissue collapse, occurred first in central interveinal areas of fully expanded leaves, which appeared water-soaked. These areas were

unable to recover on addition of molybdenum, but turgid areas rapidly recovered. Wilson (384) concluded that "scald" of beans is caused by molybdenum deficiency due to production of seed in "scald" areas. Symptoms comprise interveinal mottling followed by "scald" or necrosis of interveinal and marginal areas, which contain abundant oxidizing substances, probably nitrate.

Phaseolus multiflorus or *coccineus.* Climbing french or runner bean: Effects are similar to those in dwarf beans, but leaves tend to be small, uniformly pale yellow-green or yellow, and finally bleached with scorched, upcurled margins. Oldest leaves are affected first and wither before falling. Flower and seed production may be suppressed in the second generation. Stem elongation may be suppressed, and plants wither.

Vicia faba. Broad bean: The lower leaves are pale; when deficient seed is used margins and interveinal areas become gray and wilted or collapsed in 15 days. Dark brown or black scorching rapidly follows, while blackening appears in young leaves. Stems are almost totally defoliated. Flowering and seed production are almost completely suppressed.

Linaceae

Linum usitatissimum. Flax: Old leaves fade and wither. Young leaves are yellow-green and later brown at the tip. Flowering is decreased, and pedicels wilt about 1 inch behind the flower bud. Lower leaf scorch of flax is probably a complex effect of molybdenum deficiency and manganese excess (243).

Polygonaceae

Fagopyrum esculentum. Buckwheat: Paling, slight necrosis, and leaf cupping appeared in plants grown in a deficient serpentine soil (202).

Rosaceae

Prunus cerasifera. Myrobalan plum: Trees grown in water culture by Hoagland (186) had small leaves which showed diffuse mottling and irregular pale brown marginal and tip scorching.

Rutaceae

Citrus limonia. Lemon: Vanselow and Datta (344) grew Eureka lemon cuttings in water cultures. Symptoms appeared at 5 months in expanded leaves of each growth cycle. They were rough in texture, possibly because of enlarged oil glands, and showed diffuse rounded or oval mottled areas especially in the marginal and apical regions. These became necrotic and dried out to an irregular pale brown marginal and interveinal scorch. Margins curled upward to produce an upward-pointed outline. Leaves fell prematurely, and axillary branches were numerous. Symptoms recurred with increasing severity in successive growth cycles but did not develop subsequently in unaffected leaves of previous cycles. Plants given ammonium nitrate showed similar but less severe symptoms. Stewart and Leonard (324, 326) described the acid soil field condition in Florida known as "yellow spot" in temple orange, tangerine, sweet orange, and grape-

fruit. Trees on grapefruit rootstock are most sensitive, and those on rough lemon are less so. Symptoms appear as water-soaked areas in leaves of the early summer flush. These areas develop into large rounded or oblong yellow spots. They may occur irregularly over the leaf or in a regular row between major veins, but generally inside the leaf margins. The yellow areas may coalesce over a large part of the leaf. The affected areas may have a darker zone with a sharper outline within the diffuse spot. Trees become severely defoliated. Floyd (135) found the spots were initially stained shiny brown above and "greasy" olive-green below the leaf. Adjacent regions became yellow-green. The spongy parenchyma swelled, filling up the intercellular spaces.

Solanaceae

Nicotiana tabacum. Tobacco: Steinberg (321) grew plants in water culture. The first symptoms were crinkling and mottling of midstem leaves. These curled or twisted and developed small, necrotic, interveinal areas, which coalesced. Leaves withered from the margins and became bleached. Symptoms spread to younger and older leaves. Stem height was decreased, and flowering was delayed.

Solanum tuberosum. Potato (fig. 1C, D, E): Tuber reserves determine the severity of symptoms. The first vegetative cycle may produce no symptoms, but 2 weeks after being sown, tubers saved from previous deficiency treatment develop symptoms. Partly or newly expanded leaves become pale and show golden yellow chlorosis with occasional dull white mottling. Chlorotic areas are irregular and diffuse, but leaf margins are often darker green. Leaf margins curl upward, with irregular necrosis followed by general withering. Young leaflets and flowers turn brown and wither before opening, followed by death of the stem growing point. These symptoms recur in lateral branches. In the third cycle, plants are initially pale green. Apical leaflets of the lower leaves appear larger than those on normal plants and show marked marginal cupping, pale yellow-green interveinal chlorosis, and marginal yellowing. Margins and interveinal areas develop brown scorch. Successive leaves wither and fall. Some leaves show purple spots around leaflet margins.

In the fourth and fifth seasons, tubers saved from deficient and complete nutrient treatments were each grown in these two respective treatments. With complete nutrient, deficient and normal tubers produced normal full-yielding plants. Deficient tubers without molybdenum produced plants showing the symptoms described; normal tubers produced larger plants showing only slight symptoms. Considerable recovery without increased severity appeared in the fourth and fifth seasons, when the work was terminated. Total and tuber yields were about 45 to 60 per cent of those given complete nutrient.

Lycopersicon esculentum. Tomato (fig. 1A, B): Symptoms appear 10 to 18 days after seeds are sown. Cotyledons remain green for several weeks. Older leaves are pale with diffuse marginal and interveinal bright yellow mottling. Leaf margins curl upward, and leaflets appear "rolled." Pale brown scorching begins at the tip of the apical leaflet of the oldest leaf and spreads inward. Then distal

lateral leaflets are next involved until the whole leaf is totally withered. Leaves are affected in succession, and apical leaflet scorch appears when the first or second lateral leaflets of the next older leaf are partly withered. Plants die in 8 to 15 weeks when 10 to 15 cm. tall. In larger, less severely deficient plants, flowering and fruiting are suppressed or decreased, and minute, rudimentary, single sessile flowers may occur on the stem. Temporary recovery has no effect on the cycle of symptoms in contrast to *Brassica* crops. The observations of Arnon and Stout (28) and Mulder (252) closely agree with those described here.

Plants given ammonium nitrate show similar symptoms. Plants given ammonium sulfate, nitrite, urea, or glutamic acid show no clear symptoms, although growth is markedly reduced. Some leaflets of expanded leaves may show sudden wilting and drying out without loss of chlorophyll (185).

In serpentine soil, tomato is more sensitive than broccoli and less so than lettuce or sugar beet (202) and shows typical symptoms (353).

Sterculiaceae

Theobroma cacao. Cocoa: Young plants grown in water culture by Maskell, Evans, and Murray (235) have pale leaves, which are translucent and thin. Diffuse chlorotic interveinal mottling is followed by marginal and interveinal brown scorch. Symptoms resemble those of nitrogen deficiency except in the mottling as contrasted with general chlorosis and in the initially marginal rather than apical scorching.

Umbelliferae

Daucus carota. Carrot: Older foliage is pale yellow-green. Leaf segments scorch at the tips. Leaves wither and collapse. The symptoms are of no diagnostic value. Chlorosis and necrosis were observed in acid soil trials (202).

Apium graveolens. Celery: Foliage becomes pale green and later uniformly bright yellow, without interveinal mottling; symptoms resemble nitrogen deficiency. Leaf segment margins of older leaves later scorch, and leaves wither in parts.

CONCLUSION

Loss of chlorophyll, mottling, wilting, necrosis, and scorching symptoms are invariably associated with use of nitrate in culture experiments and are independent of presence of additional ammonia. The mottling is associated with an accumulation of nitrate or oxidizing compounds[6] and localized distribution of molybdenum (329) in the leaves. By inference, plants showing mottling and necrosis in the field are accumulating nitrate. Chlorophyll production is not decreased by molybdenum deficiency in absence of nitrate (7, 185). In some plants, for example, celery, sugar beet, and *Gramineae*, chlorosis is uniform and mottling is less noticeable. These symptoms are suggestive of nitrogen deficiency (180, 202). This response is distinct from that of true nitrogen deficiency shown

[6] References 6, 7, 165, 185, 202, 285a, 384, 385, 386, 387.

by molybdenum-deficient clovers in acid soils because of poor nitrogen fixation by the root-nodule organisms.

Brassicas are apparently unique in showing secondary symptoms most well known as whiptail, which involve younger leaves and the growing point. These symptoms are associated with partial recovery (165, 179) or intermediate levels of molybdenum (6) or provision of nitrogen in a form which bypasses the limiting effects of impeded nitrate reduction (7). The tissue breakdown is possibly associated with a defective middle lamella (7). Tomato plants also appear to require molybdenum for growth with non-nitrate nitrogen supply but remain virtually symptomless under these conditions (185). A condition termed "pseudo-whiptail" may occur in cauliflower plants due to some environmental factor (375), but at normal molybdenum levels (285a).

Leaf-marginal cupping has been related to leaf morphology (179, 202). It is presumably due to decreased marginal growth and may be either forward or backward. Plants such as cauliflower or brussels sprouts with an entire leaf show pronounced cupping, whereas those with relatively divided leaves, such as thousand head kale or rape, show little cupping or the cupping is localized. In early stages or with less severe molybdenum deficiency, some plants, for example, potato, cauliflower (6), savoy cabbage, appear to have larger leaves than normal. The tendency for cotyledons and sometimes the oldest leaf to remain normal for a long time is noteworthy.

Crop sensitivity differs. In culture experiments where absolute supplies are low and there are no problems of availability, tomato, beet, lettuce, and all brassicas show high requirements. The requirements for clovers, lucerne, carrot, and celery are markedly lower and for many cereals and grasses lower still. Beans and peas are revealed to be relatively sensitive when initial seed reserves have been depleted. The decreased sensitivity of rape (285a) and the low requirements of sorghum and sweet corn (202) when grown in soil are associated with the greater absorptive capacity for molybdenum shown by these plants. The great sensitivity of spinach (202) and lettuce (285a) may be due to poor absorptive capacity.

The characteristic appearance and high sensitivity of certain plants permits their use as indicator crops for diagnostic purposes. Cauliflower and broccoli, summer cabbage, spinach, lettuce, and tomato are the most suitable for this purpose. Citrus may be useful in tropical regions.

MOLYBDENUM DEFICIENCIES IN LEGUMES IN AUSTRALIA

ALFRED J. ANDERSON

Commonwealth Scientific and Industrial Research Organization[1]

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The role of molybdenum in the nutrition of legumes and nonlegumes has recently been reviewed (23). The present paper concerns deficiencies of this element in legumes in Australia, where many plant species, both legumes and nonlegumes, have been found to respond to molybdenum. As a fertilizer molybdenum is used principally on mixed pasture containing a legume. Its first effect is to increase symbiotic nitrogen fixation and thus the growth of the legume. Ultimately this increases the fertility of the soil and the yield of grasses and other nonlegumes.

The use of molybdenum on legumes is of particular importance in Australia because of the large land areas sown to mixed pasture containing a legume. Davies (86) has discussed the importance of these pastures in the Australian economy. By sowing pasture and applying the correct fertilizer a manifold increase in the carrying capacity for stock can be achieved and the fertility of the soils increased. This is being done mainly in southern and eastern Australia where the rainfall is more than about 15 inches a year.

Subterranean clover (*Trifolium subterraneum* L.) has been the principal legume and superphosphate the principal fertilizer used in pasture improvement in Australia. Subterranean clover is an annual legume well adapted to areas where soils are acid and annual rainfall is more than about 17 inches, and where summers are too dry for white clover (*Trifolium repens* L.). In areas where summer rainfall is more favorable white clover is sown. Alfalfa (*Medicago sativa* L.) too, is sown in some places, more particularly in areas where soils are less acid.

Nearly all unimproved soils are very deficient in both nitrogen and phosphorus. If clover is sown without superphosphate the crop fails, but superphosphate is of only limited benefit on pasture without legumes or combined nitrogen fertilizer. Superphosphate was regarded solely as a phosphatic fertilizer for this country until recently, when sulfur deficiency was found to be widespread. Responses to superphosphate are often due to both the phosphorus and the sulfur in this fertilizer (19). It is now known that in many areas there are also deficiencies of other elements.

Since molybdenum deficiency in Australia was first reported in 1942 for subterranean clover and alfalfa on an ironstone soil in South Australia (8), it has been found in many places throughout southern and eastern Australia. An important commercial fertilizer, molybdenum-superphosphate, which contains 1½ pounds of molybdenum trioxide per ton (2240 pounds) of superphosphate, is used to correct the deficiency. The mixture provides for a dressing of about

[1] Canberra A.C.T., Australia.

FIG. 1. A PASTURE THAT FAILED IN THE SECOND YEAR AFTER BEING SOWN ON AN ACID SOIL ON THE SOUTHERN TABLELANDS OF NEW SOUTH WALES

The small ash patch (center) indicates well developed subterranean clover plants; Stunted yellow subterranean clover plants either lack nodules or, when nodulated, are deficient in molybdenum

FIG. 2. SOME NODULATED, MOLYBDENUM-DEFICIENT CLOVER PLANTS THAT DEVELOPED 4 YEARS AFTER BEING SOWN WITHOUT MOLYBDENUM

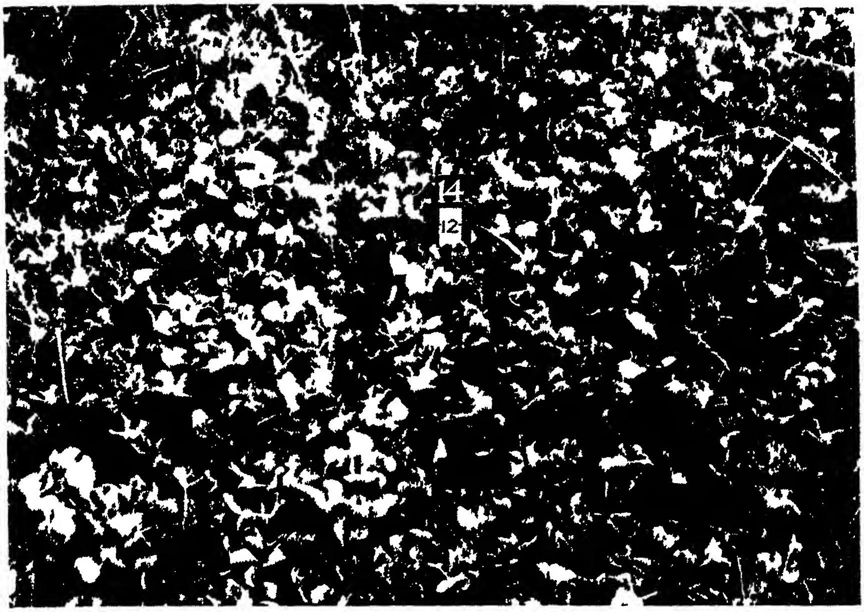

FIG. 3. NODULATED SUBTERRANEAN CLOVER, 4 YEARS AFTER BEING SOWN WITH MOLYBDENUM

This result can now be achieved by the second year if both molybdenum-superphosphate and light dressings of lime are used

2 ounces of molybdenum trioxide per acre, depending on the amount of superphosphate applied (figs. 1, 2, 3).

EFFECTS OF MOLYBDENUM DEFICIENCY

Application of superphosphate improves growth of the clover and thus increases plant requirement for molybdenum. Symptoms of molybdenum deficiency then become apparent, and responses to molybdenum occur.

The pale green color of molybdenum-deficient pastures indicates nitrogen deficiency. In fact, both clovers and grasses are deficient in nitrogen because of the low nitrogen status of the soils in relation to the phosphorus and sulfur status following application of superphosphate and because molybdenum deficiency inhibits symbiotic nitrogen fixation in clover (11, 15, 23).

Deficient clover plants have smaller than normal, pale green or yellow leaves, and stems and petioles generally show a reddish brown coloration. Stunted clover plants are nodulated and develop to maturity, producing viable seeds that maintain some plants of the species in the pasture (9). Where the deficiency is acute, the plants may measure only 1–2 cm. in diameter and in height at maturity. The paler green molybdenum-deficient plants always contain a lower percentage of nitrogen than do corresponding plants that are not deficient. For example, in an experiment on the southern tablelands of New South Wales (12) pale green untreated subterranean clover plants contained 2.5 per cent nitrogen in contrast to 3.4 per cent nitrogen in well-developed, dark green plants treated

with 2 ounces of molybdenum trioxide per acre. In addition, where molybdenum was applied, the yield of clover increased from 829 pounds to 1523 pounds of dry matter per acre.

Grasses and clovers respond to combined nitrogen fertilizers, becoming dark green and normal in growth. This response occurs even when the nitrogen treatments decrease the amount of molybdenum in the plants. The deficiency of molybdenum induces a true nitrogen deficiency in the host legume, which can be corrected by applying either molybdenum or combined nitrogen fertilizer (11, 15).

The fact that only nitrogen deficiency is induced in the clover shows that molybdenum is deficient in the clover only so far as it affects nitrogen fixation. Since the host legume requires molybdenum for growth quite apart from symbiotic nitrogen fixation, it is clear that the small amount of molybdenum which clover plants do obtain from these molybdenum-deficient soils is sufficient for metabolism in the host plant. To date, though no exceptions to this have been recorded for clover in the field, deficiencies of molybdenum for the host legume have been recorded (108, 387) for beans (*Phaseolus vulgaris*) and for peas (*Pisum sativum*). Molybdenum deficiency in the host legume is apparent where nitrogen fertilizer has been applied. There are characteristic symptoms, including necrosis of leaf tissue, quite distinct from symptoms of nitrogen deficiency. Characteristic lesions of molybdenum-deficient non-legumes are also unlike symptoms of nitrogen deficiency (15).

Since deficiency of molybdenum decreases the percentages of both protein and nonprotein nitrogen in clover plants, it decreases, therefore, the percentage total nitrogen (15). This effect is due to the decrease in the supply of nitrogen to the host plant brought about by the decrease in symbiotic nitrogen fixation. When, however, plant molybdenum is deficient for the utilization of nitrate nitrogen, although the deficiency decreases the percentage protein nitrogen, it increases the percentage nonprotein nitrogen (15). In the latter case the molybdenum-deficient plants do not have a low percentage total nitrogen, but are paler green than the treated plants. In each case the pale green color is associated with a lower percentage protein nitrogen.

An illustration of the comparative effects of molybdenum on the nitrogen content of clover, and of a nonlegume can be found in the results of Anderson and Spencer (15) with subterranean clover and flax. The results are expressed as a percentage of dry matter of plant tops. Application of molybdenum to subterranean clover increased (*a*) the total nitrogen from 2.0 to 3.0 per cent, (*b*) the protein nitrogen from 1.6 to 2.5 per cent, and (*c*) the nonprotein nitrogen from 0.3 to 0.5 per cent. Application of molybdenum to flax had no effect on the total nitrogen, which was 2.5 per cent with or without molybdenum, but it did increase the protein nitrogen from 1.4 to 1.7 per cent and decreased the nonprotein nitrogen from 1.1 to 0.8 per cent.

Clover plants deficient in molybdenum have more nodules than do normal plants (11, 15). The number may be decreased by applying either molybdenum or combined nitrogen, provided the combined nitrogen also increases the per-

centage nitrogen in the plants. This indicates that the effect on the number of nodules is attributable to the effect of nitrogen deficiency, brought about by molybdenum deficiency, in increasing the susceptibility of the plants to infection with *Rhizobium*.

In addition to being more numerous, nodules on molybdenum-deficient clover plants are also smaller and paler than those on normal plants. The smaller size of the nodules does not result, however, simply from an increase in the number of small nodules, for although molybdenum deficiency does increase the number of nodules, it also decreases the number of larger nodules (15).

Large pink nodules appear to be a symptom of vigorous nitrogen fixation within the nodule. Deficiency of molybdenum, deficiency of sulfur, and application of combined nitrogen all decrease symbiotic nitrogen fixation, and all decrease the size of the nodules (15) and reduce the amount of their pink coloration. Virtanen and Laine (349) showed that the red hemoglobin pigment is present in active nodules, and that nodules with only green pigment do not fix nitrogen. Very large pink nodules can be obtained by creating conditions unfavorable for the survival of *Rhizobium* in the soil but favorable for symbiotic nitrogen fixation.[2] This restricts the number of nodules formed on roots and increases nitrogen fixation per nodule. Conversion of red hemoglobin pigment to ineffective green bilirubin pigment can be induced by increasing the number of nodules.

The evidence thus shows that a molybdenum deficiency in pasture restricts yield and nitrogen content of clover, and hence adversely affects the quality of the pasture as a fodder for stock and limits the value of the clover for improving the fertility of the soils. The lack of response to molybdenum, of the nitrogen-deficient grasses in the pasture, apart from benefits obtained through the clover, shows that any effect molybdenum may have in these soils on nitrogen fixation by free living organisms, such as *Azotobacter*, is insignificant in comparison with its effect on symbiotic nitrogen fixation.

FACTORS AFFECTING RESPONSE TO MOLYBDENUM

Responses to molybdenum are considerably affected by variation in the supply of other elements and by variation in the soil reaction. Some treatments increase the response to molybdenum and others decrease the response.

The most important factor of practical importance in the response of legumes to molybdenum in Australia is the phosphorus and sulfur status of the soils. Where superphosphate is not applied or where the amount used is insufficient, growth of plants is restricted by phosphorus or sulfur deficiency (10, 17, 19). Under these conditions the response to molybdenum is either restricted or absent altogether.

By the use of subterranean clover in pot cultures in a glasshouse, McLachlan (231) tested the effects of phosphorus, sulfur, and molybdenum on 32 virgin soils from unimproved pasture in eastern Australia. The phosphorus, sulfur, and

[2] Unpublished data from experiments by Anderson, Meyer, and Fawcett, Commonwealth Scientific and Industrial Research Organization, Canberra A.C.T., Australia.

molybdenum were applied alone and in all combinations. Significant responses to molybdenum occurred on 12 of the soils to which phosphorus and sulfur had been applied, but no soil responded to molybdenum where neither phosphorus nor sulfur had been added.

Deficiency of sulfur inhibits protein formation in clover, and this in turn inhibits symbiotic nitrogen fixation (16). Clover plants deficient in sulfur, like those deficient in molybdenum, are pale green and have a low percentage of nitrogen. Where sulfur is deficient, the plants may respond little or not at all to molybdenum, in that they remain pale green with a low percentage nitrogen. Normal responses to molybdenum occur only where sulfur deficiency is corrected. Conversely, normal responses to sulfur occur only where molybdenum deficiency is corrected.

Sulfur deficiency is not so common or so acute as phosphorus deficiency, but it can be readily induced on most soils by applying a phosphatic fertilizer that does not contain sulfur (19, 231).

Plants deficient in phosphorus have dark green leaves, usually with a few bright yellow older leaves, depending on the nitrogen status.[3] Molybdenum deficiency becomes evident in clover after application of phosphorus has increased the growth and demand for nitrogen to the stage where the molybdenum supply is insufficient.

Deficiencies of other plant nutrients, excluding nitrogen, would also be expected to restrict the response to molybdenum. Deficiencies of boron and molybdenum occur together in places, and where the deficiencies are acute the interaction is positive. For example, in an experiment on the southern tablelands of New South Wales (18) a dressing of 2 ounces of molybdenum trioxide per acre increased the yield of clover from 868 pounds to 2036 pounds of dry matter per acre. This occurred where all the plots had been treated with superphosphate. In the same experiment, where 3½ pounds of boron had been applied with the superphosphate, the molybdenum increased the yield of clover from 948 pounds to 2894 pounds per acre. At the significance level of $P < 0.01$ the response to molybdenum in presence of boron was greater than the response where boron was not applied.

As already discussed, responses of clover to molybdenum are greater where nitrogen is deficient. Application of combined nitrogen corrects the nitrogen deficiency in the plant and decreases the response to molybdenum. The interaction is therefore negative (11, 15) and in contrast to the effect of combined nitrogen when molybdenum is deficient for the host plant (15). Deficiency of molybdenum in the host plant becomes apparent when nitrogen is not deficient, in which case the nitrogen-molybdenum interaction is positive.

The difference in the nitrogen-molybdenum interaction for a legume and a nonlegume has been illustrated by Anderson and Spencer (15), who used subterranean clover (*Trifolium subterraneum*) and flax (*Linum usitatissimum*) in pot cultures. Molybdenum increased the yield of clover from 2.8 g. to 7.4 g.

[3] Unpublished data.

per pot where no nitrogen was applied, and only from 6.3 g. to 7.8 g. per pot in presence of nitrogen. The yield of flax where no nitrogen was applied was 1.5 g. per pot without molybdenum and 1.7 g. per pot with molybdenum. In presence of nitrogen, molybdenum increased the yield from 4.1 g. to 5.6 g. per pot. In each case the interaction was significant at $P < 0.01$.

These results show that deficiency of molybdenum for nitrogen fixation in clover may be masked where the nitrogen status of the soil has been increased. Young clover plants sown on fallowed land may be dark green and may grow well until the available soil nitrogen has been depleted. Conversely, deficiency of molybdenum for metabolism in nonlegumes and in legumes without nodules would become less evident as nitrogen deficiency developed.

Lime has pronounced effects on the response of plants to molybdenum; on some soils responses do not occur if lime has been applied, on other soils responses occur only when some lime has been applied, and on still other soils lime may have little or no effect on the response to molybdenum. The nature of the effect of lime on the response to molybdenum varies markedly, depending on conditions.

A common effect of lime is to correct the deficiency of molybdenum, either partly or completely, by increasing the availability of molybdenum in the soil.[4] Anderson and Oertel (10) demonstrated this effect of lime in experiments with subterranean clover in pot cultures on a soil from Meadows, South Australia. Where superphosphate alone had been applied, 1 ounce of sodium molybdate per acre (as calculated on the basis of the pot surface area) increased the yield of clover from 5.3 g. to 15.3 g. per pot. Where superphosphate and lime had both been applied, the yield was 14.5 g. per pot with or without molybdenum. The effect and interaction were both significant at $P < 0.01$.

The effect of lime in increasing symbiotic nitrogen fixation, through its effect on the uptake of molybdenum, was shown in the same experiment by the interaction of molybdenum, lime, and nitrogen. Where superphosphate and sulfate of ammonia had been applied together, the yield was 17.3 g. per pot. Here the application of molybdenum gave 18.1 g. per pot, lime 19.3 g., and lime and molybdenum together 19.3 g. The only pale green nitrogen-deficient clover plants in the experiment were those that received no molybdenum, lime, or nitrogen. As already indicated, these plants gave a yield of only 5.3 g. per pot.

The sulfate of ammonia used in the experiment decreased the plant uptake of molybdenum whereas the lime increased the uptake. The results show that the lime actually corrected nitrogen deficiency in the plants by increasing the uptake of molybdenum and hence symbiotic nitrogen fixation. The effect of lime on color, nitrogen content of the plants, and nodulation was similar to the effect of molybdenum.

The effect of lime on the availability of molybdenum is of practical significance in Australia only insofar as the lime increases the availability of the molybdenum already present in the soil. Molybdenum applied to unlimed soil as

[4] References 10, 139, 267, 276.

sodium molybdate or as molybdenum trioxide at 1 or 2 ounces per acre corrects the deficiency, and a single dressing remains fully effective for at least 6 years (18).

The extent to which the application of lime corrects molybdenum deficiency varies considerably, and depends on the amount of unavailable molybdenum present in the soil. The marked responses of clover to molybdenum and lime in the experiments discussed were obtained on a soil from Meadows which contained about 10 ppm. of molybdenum (10). About 25 miles away, on a soil at Houghton, lime had no significant effect on yield or on colour of molybdenum-deficient subterranean clover plants in the field (9). In pot cultures lime increased the yield of clover on this soil from 2.6 g. to 3.7 g. per pot, whereas molybdenum increased the yield to 5.0 g. per pot without lime, and to 5.4 g. per pot in presence of lime (10). The soil at Houghton contained less than 1 ppm. of molybdenum, which indicates that the small response to lime on this soil was due to a low content of unavailable molybdenum.

Improved nodulation of clover plants (13, 21, 314) is a common effect of lime which results from an increase in the survival of *Rhizobium* in the soil (21, 314). This is quite distinct from the effect of lime in increasing the uptake of molybdenum. Where the soils are more acid than about pH 5.5, clover sown on new land often fails to form nodules even when the seed is inoculated, and such unnodulated clover plants do not respond to molybdenum (21). Normal heavy dressings of lime will counteract the soil acidity and induce nodulation, and depending on conditions may also release sufficient molybdenum from the soil. The same beneficial effect on nodulation can be obtained with as little as 200 pounds of lime per acre, provided the inoculated clover seed is mixed with the lime when sown. Normal growth of clover can be obtained on these molybdenum-deficient acid soils by using molybdenum-superphosphate at the time of sowing, and by drilling the inoculated clover seed with 200 pounds of lime (calcium carbonate) per acre. On the soils concerned, annual dressings of lime or molybdenum are not required.

The effects of a light dressing of lime in inducing clover nodulation and increasing response to molybdenum, and the effect of a heavier dressing in increasing the uptake of molybdenum from the soil, are illustrated by the following results obtained in an experiment on a soil of about pH 5.0 (21). Where no lime was applied clover plants were pale green and did not respond to molybdenum. The yield obtained on unlimed plots was only 336 pounds of dry matter per acre, with or without molybdenum. Where a dressing of 224 pounds of lime (calcium carbonate) per acre was applied, response to molybdenum was marked. Here 2 ounces of molybdenum trioxide per acre raised the yield of clover from 2128 pounds to 4144 pounds of dry matter per acre. The yield obtained with the combined treatment of 224 pounds of lime per acre and molybdenum was equal to the yield of 4144 pounds per acre obtained also where 896 pounds of lime per acre was used with molybdenum. Where 896 pounds of lime per acre was applied without molybdenum, the clover grew well and produced 3920 pounds of dry matter per acre.

GENERAL ASPECTS OF MOLYBDENUM DEFICIENCY IN PASTURE

Plants growing in unimproved native pasture show no visual symptoms of molybdenum deficiency primarily because of their deficiency of other elements, particularly phosphorus, sulfur, and nitrogen for the nonlegumes, and phosphorus and sulfur for the legumes.

Many of the unimproved native pastures contain a sparse population of herbage legumes (of the *Trifolium* and *Medicago* species) severely stunted by deficiencies of phosphorus or sulfur. Similarly, subterranean clover or other legumes sown on new land without superphosphate are stunted by phosphorus or sulfur deficiency and not by molybdenum deficiency.

The evidence already discussed, particularly that of McLachlan (231), shows that phosphorus and sulfur deficiencies are so severe that molybdenum is, in fact, not deficient for plants growing on our untreated soils. Since molybdenum becomes deficient only when other deficiencies are corrected, it follows, therefore, that on untreated land variation in soil molybdenum status would have no effect on the ecological association of plants growing there.

The greater response of legumes to molybdenum does not necessarily imply that legumes have the greatest requirement for this nutrient. Deficiency of nitrogen severely restricts growth of other plants, and this in turn limits their response to molybdenum.

A general feature of newly developed country severely deficient in molybdenum is the occurrence of vigorous dark green clover plants in patches where trees have been burned. The ash may contain about 10 ppm. of molybdenum (10). Therefore, apart from increasing the pH of the soil, the ash adds significant amounts of available molybdenum, and may correct molybdenum deficiency even on soils where lime is not effective. A similar effect of ash can occur, however, for other reasons, particularly by counteracting soil acidity (13, 314) and thus improving clover nodulation.

Since sulfur deficiency and defective nodulation of clover roots also induce nitrogen deficiency symptoms in the clover plants, in the field they may be confused with molybdenum deficiency. Both problems may occur in country where molybdenum is deficient (16, 21). Sometimes sulfur deficiency can be detected by observing effects that have been obtained with superphosphate, which corrects sulfur deficiency but intensifies molybdenum deficiency where it increases growth of the clover. Defective nodulation can usually be detected by the occurrence of scattered green plants that have become nodulated, but if molybdenum deficiency is severe this effect is masked. Inspection of roots may disclose an absence of nodules, or the presence of small nodules. But the latter condition may result from molybdenum deficiency, or from sulfur deficiency or from infection with an ineffective strain of *Rhizobium*.

Where the deficiency is not severe, nitrogen-deficiency symptoms are often difficult to detect visually. The paler green color often becomes apparent only when there is control plot alongside the molybdenum-treated plot to compare it with. The use of visual symptoms for diagnosis of molybdenum deficiency in clover, therefore, has only a limited practical value.

Since molybdenum in the clover is deficient for symbiotic nitrogen fixation, it seems unlikely that the molybdenum content of plant tops could provide an accurate guide to molybdenum requirements. Apparently the minimum concentration of molybdenum needed in the plant tops varies considerably (10, 15). Plants with 0.5 ppm. of molybdenum in the dry matter of the plant tops are not likely to be deficient; a concentration of 0.1 ppm. is sometimes sufficient. In studies with alfalfa in sand culture, Jensen (197) found that the nodules contained much more molybdenum than did the tops, and the amount of nitrogen fixed was restricted when the nodules contained 3 to 10 ppm. of molybdenum. Possibly concentration of molybdenum required in the nodules is progressively influenced by the nitrogen requirement of the plant, the highest concentration being needed where there is the greatest demand for nitrogen. The present writer has observed that where molybdenum deficiency is slight, responses to molybdenum may disappear as the fertility of the soil is increased by the growth of clover.

The evidence on the effects of various treatments on the molybdenum response, as already discussed, shows that care must be taken to select the right conditions when testing for field responses of clover to molybdenum. In general, deficiencies other than molybdenum need to be corrected, but the response may be prevented if nitrogen or lime is applied. On the other hand, some lime may be needed. Methods of taking these factors into account in a field test for deficiencies have been described (20, 21).

Molybdenum deficiency does not occur in well-defined areas but is scattered in places throughout most of the areas where clover is being sown. Molybdenum is a very inexpensive fertilizer, and in many areas it is now becoming standard practice to use molybdenum-superphosphate in place of ordinary superphosphate in the first year of sowing to insure the new pasture against an occurrence of molybdenum deficiency.

MOLYBDENUM DEFICIENCY IN HORTICULTURAL AND FIELD CROPS

P. R. STOUT AND C. M. JOHNSON

University of California[1]

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Because "whiptail" foliar symptoms (now known to be molybdenum-deficiency symptoms) in cauliflower and broccoli are so obvious and yield increases so dramatic when molybdenum is supplied or made available by liming, molybdenum nutrition of these plants has been studied in greater detail than that of most other plant species.

Whiptail disease of broccoli and cauliflower appears to have been recognized in 1924 in New York State by Clayton (67). During the next 17 years the disease was further studied in New York State by Wessels (371) and Underwood (342), in New South Wales by Magee (232), in Victoria by Stubbs, (332), and in Fiji by Parham (271). These investigators believed the cause of disease to be the unavailability of some soil nutrient, and the cure, liming.

Perhaps the earliest recognition of a plant disease now known to be associated with molybdenum deficiency is yellow spot on citrus in Florida, which Stewart and Leonard (324) reported was recognized 50 years ago.

In 1939 Arnon and Stout (28) demonstrated that molybdenum was an essential element for the nutrition of the tomato plant, and in 1940 Piper (273) showed the element necessary for growth of oats.

Whiptail disease of cauliflower and broccoli was shown by Davies (80) and Mitchell (244) to be a molybdenum deficiency. Many workers have adequately demonstrated, both in greenhouse experiments and field trials, that whiptail is in reality an uncomplicated molybdenum deficiency which can be cured in all instances by application of minute amounts of molybdate to either foliage or soil.[2] Hewitt and Jones (165), Mulder (252), and Waring *et al.* (362) have published excellent illustrations of molybdenum-deficient cauliflower and other plants.

Field responses to molybdenum by Brassica crops have been reported from widely separated geographic areas. Australia and New Zealand are represented in the greater number of instances. Reports of molybdenum deficiencies from Queensland have been made by Morgan and Henderson (246) and Von Stieglitz and Chippendale (350)[3]; from New South Wales by Magee[3], Waring (364),

[1] Berkeley, California. This review was prepared while the authors were Fulbright Research Scholars in Australia, P. R. Stout at the C.S.I.R.O., Division of Biochemistry and General Nutrition, and C. M. Johnson at the Waite Agricultural Research Institute, Adelaide, South Australia. The assistance of Miss S. J. Susman, librarian of the Waite Agricultural Research Institute, and Miss E. E. Wardlaw at the Division of Biochemistry and General Nutrition is gratefully acknowledged.

[2] References 109, 113, 144, 165, 179, 184, 191, 202, 205, 227, 244, 246, 252, 278, 280, 281, 289, 332, 350, 351, 362, 364, 385, and footnotes [3] and [4].

[3] Personal communication, 1955.

Waring *et al.* (362), and Wilson and Waring (385); from Tasmania by Wade (351); from Victoria by Stubbs (332); from South Australia by Botting (53); and from Western Australia by Dunn and Jones (109). Davies (80), Lobb (227), and Mitchell (244) reported molybdenum deficiencies from New Zealand, as did Parham (271) from Fiji. Reports from the United Kingdom include those of Jones and Dermot (205) and Plant (278, 280, 281). Mulder (252) reports molybdenum deficiency from Holland. In the United States reports of whiptail occurrences have been confined to eastern coast areas, namely in Florida, by Eddins *et al.* (113) and Gammon *et al.* (144); in New Jersey by Bear (36); in New York by Clayton (67), Raleigh (289), Underwood (342), and Wessels (371).

As a practical control, on some acid soils, where total molybdenum is fairly high but present in plant-unavailable form, liming does suffice to overcome the deficiency, which is in accord with the many observations cited that whiptail disease can usually be cured by liming the soil. The release of molybdenum from the unavailable form in acid soils has been explained in part through the participation of molybdates in anion exchange. Stout *et al.* (330) cited experiments in which anion exchange behavior of molybdate and hydroxyl ions on halloysite columns was demonstrated. Direct applications of a few ounces of molybdate per acre—usually as molybdenized phosphate—also supplies plant requirements for the element.

Generally, on molybdenum-deficient acid soils, liming offers other benefits, such as aiding nodulation of legumes. The economics of management of molybdenum nutrition, therefore, ranges between the application of several hundredweight of lime alone and the direct application of a few ounces of molybdenum.

Molybdenum treatments of horticultural and field crops must take into account relations of molybdenosis (teart disease) in crop production and livestock problems.[4] Molybdenosis results from ingestion of excessive amounts of molybdenum by ruminants. In New South Wales Waring *et al.* (362) recommended the control of whiptail in cauliflowers by watering the plants with a solution of 1 ounce of ammonium molybdate in 10 gallons of water per 10 square yards of seed bed 1 or 2 weeks before transplanting. Gammon *et al.* (144) suggested use of varieties of cauliflowers less susceptible to molybdenum deficiency; liming the soil to as high pH as compatible with other crops (for example, potatoes) grown in the rotation; and use of fertilizers that do not give rise to physiological soil acidity. By these recommendations the risk of building up molybdenum concentrations in foliage, which might serve as feed for ruminants, is lessened. Davies and Grigg (84) especially cautioned against the use of excessive amounts of molybdenum on peats and copper-deficient areas.

As suggested in the whiptail disease of cauliflower, molybdenum deficiency is displayed more prominently by some species than others. To get direct comparison of species response to molybdenum, Johnson *et al.* (202) grew in a California soil 30 different types of crop plants in pots all containing the same low-molybdenum soil and under a common cultural environment. This soil, discovered by Walker (353) to be low in molybdenum, was derived from serpentine. Its

[4] References 59, 72, 128, 224, 357.

soil paste pH was 6.8 as taken from the field, and it contained less than 1 ppm molybdenum by fusion analysis. This soil was assumed to be uncomplicated by a large supply of nonavailable molybdenum, so that relative responses to molybdenum fertilization as between species could be observed directly. For similar studies, Mulder (252) used an acid ironstone-containing soil between pH 5 and 6 and an acid lowmoor soil. Spinach gave the highest response to molybdenum fertilization in each instance. On the neutral soil (202) no response was obtained to graminae—wheat, sorghum, oats, barley—but on the acid soils (252) oats and wheat did respond to molybdenum fertilization. All Brassica and Chenopodiacae crops and lettuce and tomato plants were relatively sensitive to added molybdenum. When nitrogen was supplied, representative legumes were adequately supplied by the native soil molybdenum (202, 252), but if the legumes were not given fixed nitrogen, addition of molybdenum resulted in marked increases in yield (252).

Greenhouse studies, in cultures, require the most refined chemical methods of purification to demonstrate molybdenum deficiencies in plants. Nutrient cultures, however, have been used successfully in the demonstration of a molybdenum requirement for a number of species. Experimental plants have included alfalfa (117), beans and peas (184, 237), brassicas,[5] citrus (344), lettuce (29), oats (273), plum (186), tobacco (321), and tomato (28, 165, 247).

Experience with the difficulties in preparing laboratory culture media sufficiently free from traces of molybdenum to demonstrate molybdenum deficiency in plants make very widespread field occurrences of the disease appear to be remarkable. Nevertheless large areas of land mostly in Australia and New Zealand, involving some millions of acres, have been implicated. From the point of view of agricultural economics, the secondary role of molybdenum in nitrogen fixation by pasture legumes assumes the greater importance, but many other nonlegume crop plants have been found under field conditions to respond to molybdenum fertilization.

REPORTS OF MOLYBDENUM DEFICIENCIES IN CROP PLANTS

Alfalfa has been shown to respond to molybdenum supplements in purified solutions (117) and in soil pots as well as in four of six field trials in New Jersey (119). Young and Takahashi (392) reported yield responses in alfalfa trials in Hawaii, with considerably increased yields in protein and total yield of several varieties of lucerne. Since their plots received heavy applications of nitrogen, the molybdenum response appears not to have resulted from a secondary stimulation of nitrogen-fixing microorganisms. During the longer summer days, molybdenum additions resulted in a daily increase of as much as 100 pounds of dry feed per acre.

Beans have been interesting as another legume grown under field conditions where the molybdenum supply was so low that the deficiency was a direct one for the plant (as distinct from a secondary problem of nitrogen fixation). Wilson (387) first drew attention to scald disease of beans as a molybdenum deficiency.

[5] References 165, 179, 180, 184.

He observed that plants from seeds imported into areas (near Sydney) of scald disease occurrence were normal but plants from local seed developed scald disease, and it was suggested that the immunity of imported seed could have been provided by molybdenum reserves in the seed. Meagher *et al.* (237) and Hewitt *et al.* pointed out (184) that reserves of molybdenum in seed can be adequate to supply the plant originating from the seed with the entire complement needed to complete its growth and development.

Magee[6] reported that the molybdenum-deficient areas in New South Wales are being located as a part of the regular program of seed certification. When instances of scald disease of beans are brought to its attention, the New South Wales Department of Agriculture knows that first of all the field carrying the plants is low in molybdenum and that the field of the seed's origin is also low in molybdenum. Other field responses to molybdenum with beans have been reported by Lobb (227) in New Zealand and Von Stieglitz and Chippendale[7] in Queensland.

Brassica crops in addition to cauliflower (discussed separately because of its special agricultural significance) seem to have more pronounced molybdenum requirements than most other plant families;[8] but as with the Chenopodiacae, few field observations of molybdenum deficiency have been recorded. Lobb (227) obtained field symptoms where molybdenum deficiency was observed for rape, kale, chou moelier, turnips, swedes, and radish. Rape, chou moelier, kale, and turnips showed acute symptoms and Lobb's descriptions parallel closely the foliar manifestations of the disease as observed under greenhouse laboratory conditions.

Carrots responded to molybdenum applications in field trials in New Zealand (227).

Celery, when deficient in molybdenum, has thin and unusually solid stalks. When, as sometimes, the stalk is nearly pure yellow, is has a high nitrate content. The disease has been observed particularly (350)[7] in celery grown in Queensland where fields have been replanted for a number of years with local seed.

Citrus: Stewart and Leonard (324) reported that a disease known as "yellow spot", which had been known in Florida for nearly 50 years, could be cured by foliar applications of molybdenum. The symptoms of yellow spot first appear in early spring as water-soaked areas in leaves. These areas develop in summer into large interveinal yellow spots with green color on the lower surface. When the lower part of the tree was sprayed with 0.1 ounce of sodium molybdate in 10 gallons of water, the sprayed parts turned green, but the upper leaves of the tree remained yellow and eventually dropped. Concentrations of 0.03 to 0.08 ppm. Mo were found in yellow spot leaves, with slightly higher values in green leaves from adjacent plots the soil pH of which had been raised through liming from 4.2 to 5.6. In comparison, Vanselow and Datta (344), reported 0.02 to 0.03 ppm Mo of dry matter for severely affected leaves of molybdenum-deficient citrus grown

[6] Personal communication, 1955.

[7] Personal communication, Von Stieglitz and Chippendale, 1955.

[8] References 165, 179, 202, 252.

in water cultures. Molybdenum did not appear to be readily translocated in the trees.

Chenopodiaceae, as represented by sugar beet, table beet, and chard, are fairly sensitive to molybdenum supply (180, 202, 252), as shown in greenhouse laboratory studies. Lobb (227) reported molybdenum responses in mangolds, silver beet, and chard in field trials on a highly molybdenum-deficient New Zealand soil where paleness and stunting were the only definite symptoms.

Cucurbits generally are considered susceptible to low molybdenum supplies. Cucumbers, pumpkins, and choko have all given rise to severe restriction of growth in areas about Brisbane. The deficiency is readily overcome through molybdenum fertilization and has been of high economic significance in the areas involved (350).[7] Rock melons (*Cucumis melo* L.) have been severely inhibited in field situations because of low soil molybdenum, but the treatment of each hill with 0.01 to 0.1 g. of sodium molybdate resulted in improvement and marked reduction of nitrate content of leaf tissue (350, 386).

Flax has been shown by Anderson and Spencer (15) to respond to molybdenum in pot tests with soil but only in presence of heavy dressings of manganese. Millikan has also described a manganese-molybdenum antagonism in soil pot trials with flax (243*a*, *c*).

Hops, having concentrations of 0.02 ppm. in the leaves, were noted by Askew (65*a*) to have yellow shoots upon emergence from the ground. The disease also resulted in white interveinal breakdown of laminae. Sodium molybdate, applied at a rate of 8 ounces per acre, corrected the disease; although ground limestone was found helpful, it was not so effective as the molybdenum.

Lettuce under low molybdenum status, but otherwise fertilized, has been reported to have no market value in some fields near Brisbane.[7] Wilson (384) described the disease as a yellowing of outer older leaves and, in a few cases, death of the interveinal areas. Formation of hearts was delayed. Strongly affected plants lost all semblance of the lettuce structure characteristic of commercial varieties. The disease was overcome through molybdenum applications. Plant (285) observed molybdenum-deficient lettuce in England in a field which produced whiptail disease in cauliflower. In Plant's experiments the very high rate of 4 pounds molybdenum per acre was required to overcome the deficiency completely. Rubins (303), with pot tests of selected native soils from Connecticut, found that lettuce yields could be considerably increased through applications of molybdenum or lime. Where liming was light and phosphate dressings were heavy, the symptoms were compatible with those described by Wilson (384). From the few field experiments reported, the molybdenum requirement for lettuce appears to be especially high, comparable perhaps to that of the Brassica crops. Johnson *et al.* (202) has rated the molybdenum requirement of lettuce as relatively greater than that for the Brassica species.

Parsnips have been shown by Lobb (227) to respond to molybdenum under field conditions. The symptoms of low molybdenum in the parsnip plant have been described as yellow color and very stunted growth.

Peas, when grown on a Tasmanian soil of the acid ironstone type, were ob-

served by Fricke (139) to respond to molybdenum fertilization in the field. Treatment with 2 ounces to 1 pound ammonium molybdate per acre has been profitable. Later Wade (352), noting field peas to be apparently nitrogen deficient, found that sprays of ¼ ounce sodium molybdate in 3 gallons would rectify the condition, the severity of which had resulted in some crop failures. Drake and Kehoe (108), in Victoria also corrected an apparent nitrogen deficiency of peas by spraying before early flowering with solutions containing ½ ounce ammonium molybdate per gallon. The peas that showed disease symptoms correctable by molybdenum applications had been fertilized with ammonium sulfate, whereas peas that had not received nitrogen fertilizer did not respond. From these observations of Drake and Kehoe, the rhyzobium populations appeared to be little involved. Blomfield (44) reported other types of results in New Zealand. A variety of methods of application were tried including preemergence spray, postemergence spray, seed dusting, and the use of molybdenized superphosphate. Regardless of method of application, pea plants responded with better color, higher yields, and earlier maturity. Blomfield concluded from root and nodule development that the effectiveness of molybdenum was primarily on the symbiotic root organisms rather than on the plant itself. Crofts (71) also concluded that molybdenum responses to field peas in New South Wales were due to increased ability to fix nitrogen.

Since peas and beans, because of their large seeds, may contain adequate molybdenum reserves to meet the requirements of growing plants,[9] there might be field situations with peas in which the molybdenum stored in seeds would suffice for needs of the pea plant as it had for scald disease of beans. Such complexities make field interpretations more difficult.

Potatoes, as noted by Bear (36), have responded mildly to field fertilization in New Jersey through applications of foliar spray containing molybdenum. Growth increases of potatoes were obtained in greenhouse trials when before being planted the seed pieces were dipped into a 0.05 per cent solution of sodium molybdate.

Roselle (*Hibiscus sabedariffa*), though not of great importance economically, has nevertheless been of local interest in Queensland where the heart of the flower is used as an ingredient of jam. A disease, resulting in collapse of the massive central portion of the flower, was corrected through molybdenum fertilization.[10]

Roses in the same area have been severely afflicted with die-back of young growth and extreme leaf chlorosis. Correction of the molybdenum deficiency is made by leaf sprays containing 1 ounce of ammonium molybdate to 6 gallons of water (350).

Tomatoes characterized by interveinal chlorosis and cupping of older leaves have been reported by Bear (36), though the extent of the area involved was presumably limited to a small acreage. Molybdenum deficiency in commercial glasshouse tomato crops has been reported in New South Wales (25).

Tobacco culture in Queensland frequently makes use of molybdenum fertiliza-

[9] References 184, 237, 252, and footnote [3].

[10] Personal communication, Von Stieglitz and Chippendale, 1955.

tion, the recommended treatment being ½ pound ammonium or sodium molybdate per acre applied with the planting mixture (350). In these areas an increasing frequency of molybdenum deficiency in tobacco with changing cultural methods has also been noted. An older practice within Queensland tobacco-raising areas has been to grind termite mounds, place this material on seedbeds, and ignite it to sterilize the seedbeds and, incidentally, to add nutrients. Recently, supplies of termite mounds for this purpose have diminished, and with use of commercial fertilizers the need for direct molybdenum fertilization has increased.[10]

RESPONSES OF CEREALS AND GRASSES TO MOLYBDENUM

Cereals and grasses fall generally into a class of plants less sensitive to soils with restricted molybdenum supply or availability, particularly as compared to the crops discussed. It is clear, however, from Piper's early work, (273) that without molybdenum oats could not complete their life cycle, since the grain of molybdenum-deficient oats consisted entirely of empty husks. Experiments of Johnson *et al.* (202) on a low-molybdenum soil showed no response to oats, wheat, sorghum, barley, and sweet corn, though all dicotyledenous nonlegumes tested showed molybdenum responses in the same soil during the same controlled greenhouse experiments. It is not known whether the molybdenum requirement of the Gramineae is lower, or whether these plants are extracting at critical periods enough of the element from the soil to meet their physiological demands during growth. From plant analysis the molybdenum concentrations in Gramineae were: barley, 0.03 ppm.; oats, 0.03 ppm.; wheat, 0.03 ppm.; sweet corn, 0.07 ppm.; and sorghum, 0.11 ppm.; none of these latter plants showed molybdenum-deficiency symptoms. By comparison, dicotyledenous plants in the same experiment which showed acute low molybdenum stress, had molybdenum concentrations for table beets of 0.05 ppm., for sugar beets of 0.13 ppm., and for tomatoes of 0.13 ppm. When total amounts removed by the crops were calculated, there was overlapping between amounts of molybdenum removed by plants adequately supplied (Gramineae and legumes) and amounts removed by other species showing molybdenum deficiency. In ascending order, the micrograms of molybdenum removed by 8 weeks' cropping on 1,600 g. of soil are (italics indicate plants showing molybdenum-deficiency symptoms): *table beets*, 0.07; wheat, 0.11; oats, 0.17; barley, 0.28; *sugar beets*, 0.37; cowpeas, 0.67; white Dutch clover, 0.83; *tomato*, 0.87; sorghum, 1.16; and sweet corn, 2.43. These figures were obtained by deducting the molybdenum supplied by seed from the total in the plant after harvest.

Even though the Gramineae seem least demanding of soil with respect to needed molybdenum supplies, uncomplicated molybdenum deficiencies have been observed on soil-grown plants in the field and in greenhouse pots. The first demonstration was by Stephens and Oertel (322) in pot trials with Cressy shaley clay loam in which perennial ryegrass responded to molybdenum applications. Fricke (142) in Tasmania showed that the "blue chaff" disease of oats, characterized by a bluish coloration of the outer glumes and pinched grain, was a molybdenum deficiency as manifested in the field. Control of the disease was

obtained from applications of 2 ounces of sodium molybdate per acre. Fitzgerald (134) of New Zealand obtained field responses in two trials with oats through applications of 2½ ounces and 5 ounces of sodium molybdate as foliar spray per acre. Lobb (227) has also reported field responses by oats.

In New South Wales Noonan (265) noted molybdenum-deficiency symptoms in maize on a farm where molybdenum deficiency in curcurbits had been observed. The molybdenum deficiency of the maize did not result in greatly reduced yields, and untreated plants were able to overcome deficiency symptoms of the early growth period. These observations on field-grown maize parallel many greenhouse experiences by the writers, wherein plants at first markedly exhibiting symptoms of molybdenum stress may in a month or so show definite signs of recovery without molybdenum fertilization. Mulder (252) in an experimental field test with wheat, described molybdenum-deficient early plants as chlorotic and much restricted in growth. In later stages, however, color differences almost disappeared, though ear emergence was much retarded and "deaf ears" were common in the untreated wheat. Mulder (252) and Lobb (227) have noted pale yellow coloration of oats and stunting of early growth, the differences becoming less marked as the season progressed. Lobb (227) has made similar observations for wheat; rye; corn; perennial, short-rotation, and Italian ryegrasses; cocksfoot; crested dogstail; timothy; and *Phalaris tuberosa*.

Barley occupies a unique place among the Gramineae in that no molybdenum response in soil has been reported. Three different investigators have included barley in comparative experiments on molybdenum-deficient soils, and each has noted that this plant showed no response (202, 227, 252). Hewitt and Bolle-Jones (180), however, described molybdenum-deficient barley grown in purified sand cultures.

MOLYBDENUM DEFICIENCIES IN THE UNITED STATES

E. J. RUBINS

Storrs, Connecticut, Agricultural Experiment Station

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Interest in the discovery and evaluation of molybdenum deficiencies has been rapidly increasing in recent years. This paper reviews the situation in the United States and is based in part upon unpublished material generously contributed by many research and Extension Service workers.[1]

The first reported recognition of soil deficiency of molybdenum in the United States was made by van Niel (343) in 1935. He found that some sandy, slightly alkaline soils from the Monterey Peninsula of California contained insufficient molybdenum to support nitrogen fixation by *Azotobacter*. Walker (353) was the first in this country to demonstrate molybdenum deficiency for soil-grown higher plants. He found that tomatoes growing in a greenhouse on California soils derived from serpentine parent materials showed deficiency symptoms and that the symptoms disappeared with molybdenum applications. He also found that Romaine lettuce responded to molybdenum on one soil tested.

In two other crops, symptoms now known to be caused by molybdenum deficiency were reported many years before the essentiality of the element for higher plants was first shown by Arnon and Stout (28) in 1939.

The first, yellow spot of citrus, which was reported by Floyd in 1908 (135), was shown in 1952 by Stewart and Leonard (324) to be caused by molybdenum deficiency. Floyd carefully described the morphology of affected leaves and noted that the condition was not confined to any particular kind of citrus, that it was widely distributed in Florida, that it was affected by climatic conditions, and that there had been no reports of its presence prior to the freeze of 1894–95 (136). Knorr and Wander (211) reviewed the history of this condition.

The second, whiptail of cauliflower, was related to molybdenum deficiency in soils by Davies (80) in New Zealand in 1945. Unlike yellow spot of citrus, reported only in Florida and the Isle of Pines (291), whiptail was known to have occurred in other parts of the world including the United States. Clayton (67) reported the condition to be serious on soils of Long Island, especially on land used also for growth of potatoes. He and others (342, 371) observed the beneficial effect of lime in overcoming the condition and noted that some varieties and strains were more susceptible to whiptail than were others.

FIELD OBSERVATIONS

Molybdenum deficiencies observed in the field in the continental United States are summarized in table 1. Most reports have come from states along the Atlantic and Gulf coasts, but there are some notable exceptions: legumes have responded

[1] The author wishes to thank particularly C. H. Kline and G. S. Cripps of the Climax Molybdenum Company for suggestive sources of unpublished material.

TABLE 1

Field observations of molybdenum deficiency in the United States

State	Locale	Crop	Description	Source of Information*
Rhode Island	Newport	Cauliflower	Two sporadic observations of whiptail	J. B. Smith
New York	Suffolk Co., L. I.	Cauliflower	Whiptail occurs only on soils of pH < 5; more likely to occur after early potatoes	W. G. Been
	Ithaca	Cauliflower, cantaloupe	Both crops gave marked response to Mo on Dunkirk silty clay loam; whiptail of cauliflower at pH < 5	(289) C. J. Raleigh
	Rochester	Cauliflower, broccoli†	Whiptail on silt loams of lacustrine origin at pH 6.4 to 7.4	C. B. Sayre
New Jersey	Sussex Co.	Alfalfa	Significant response to Mo on 4 out of 6 silt loams at pH 6.0 to 6.8	(119)
	Middlesex Co.	Alfalfa		E. R. Purvis
	Union, Burlington Co.	Cauliflower Tomato	Whiptail at pH 5.5	E. R. Purvis (36)
Pennsylvania	Potter Co.	Cauliflower†	Whiptail suspected on potato soil of low pH	L. F. Marriott
Delaware	Dover	Cauliflower	Five instances of whiptail on Sassafras sandy loam	R. F. Stevens
Maryland	Garrett Co.	Cauliflower	Whiptail occurs on loams, silt loams, and clay loams at pH 6, especially if fertility level is high and growth vigorous	F. C. Stark R. L. Winklepleck
	Eastern shore	Tomatoes†, snapbeans†, cantaloupe†	Suspected deficiencies on acid sandy loams and loamy sands	F. C. Stark
West Virginia		Cauliflower	Whiptail occurs from pH 5 to near neutrality on soils representing variety of textures	M. E. Marvel C. B. Sperow
Ohio	Marietta area	Cauliflower, broccoli	Whiptail occurs at pH 4.7 to 5.3 on Chenango sandy loam	W. N. Brown
North Carolina	Raleigh	Cantaloupe	Deficiency on Norfolk sandy loam at pH 5 corrected by Mo spray	(118)
	Wilmington	Lettuce	Deficiency at pH 5 corrected by Mo spray	(118)

TABLE 1—Continued

State	Locale	Crop	Description	Source of Information
South Carolina	Piedmont area	Alfalfa	Mo applications to moderately acid Lloyds sandy loam corrected yellow foliage and increased yield and crude protein content	M. M. Philippe W. R. Paden
Florida	Entire citrus area	Citrus	Yellow spot appears to be associated with use of acid fertilizers; severity of deficiency varies from year to year	(135, 136, 211, 324)
	Hastings area	Cauliflower	Whiptail occurs on flatwoods sands at pH 5 or below	(112, 113)
	Sanford area	Hibiscus, sweet potato	Deficiencies occur on acid sands at pH 5.0 to 5.5; corrected by Mo applications to soil or foliage	P. J. Westgate
	Ruskin and Fort Pierce areas	Cauliflower, broccoli, tomato	Deficiencies occur on acid flatwoods sands but are becoming less common as many growers include Mo in sprays or fertilizers	B. Wolf
Louisiana	Plaquemines Parish	Cauliflower	Whiptail on alluvial soils at pH 5.3 to 6.0 especially if nitrogen and moisture levels favor good growth	R. T. Brown
	Chalmette	Cauliflower	One case of whiptail on fine sandy loam of alluvial origin	J. C. Schwegmann
Texas	Rio Grande plain	Various legumes		C. L. Shrewsbury
Wisconsin		Canning peas† Red clover†	Deficiency may occur on soils below pH 6.5 Deficiency may occur on clover-potato rotations in northern Wisconsin	K. C. Berger K. C. Berger
Idaho		Alfalfa†	Deficiency may occur on soils of pH 5.5 to 6.2 on cut-over timber land or land of timber-prairie transition	C. O. Baker
Washington	Northeastern area	Alfalfa, sweet clover, canning and seed peas	Mo fertilization significantly increased yield and protein content on Palouse loess and on soils from residual parent materials at pH 5.6 to 6.4	H. M. Reisenauer

* Contributors of unpublished information are listed by name.
† Deficiency suspected.

to molybdenum treatment in northeastern Washington[2] and on calcareous soils in southern Texas.[3]

Most difficulties have occurred on acid sandy soils, but whiptail in cauliflower has been observed on fine-textured soils in West Virginia,[4] western Maryland,[5, 6] and central and western New York (289),[7] and alfalfa has responded to molybdenum on silt loams in Sussex County, New Jersey (119). The pH of the New Jersey soils ranged from 6.0 to 6.8, and most of them were derived from calcareous parent materials. At least some and perhaps all of the silty clay loams and silt loams on which whiptail has been reported from western New York are derived from calcareous lacustrine deposits.

Though most of the instances concern alfalfa and cauliflower, deficiencies have not been confined to these crops. Other crops reported were broccoli, lettuce, cantaloupe, tomato, sweet potato, and various legumes including canning peas and red clover. Yellow spot of citrus deserves special mention. It has been observed on all varieties of citrus in virtually every part of the citrus-growing area of Florida and represents the only known molybdenum deficiency involving trees growing in soil (324). Sprays containing soluble molybdates are effective in controlling yellow spot (325). For control of whiptail, sprays and soil applications have been recommended, but the condition has often been prevented by judicious use of lime and planting of whiptail-resistant varieties.

GREENHOUSE EXPERIMENTS

Experiments on molybdenum-deficient soils have also been conducted as greenhouse pot studies. Some have been carried out in conjunction with the field observations given in table 1; others represent independent studies in states that have not yet found field deficiencies.

Walker's (353) early work with tomato and lettuce was conducted in a greenhouse on primary soils from the serpentine barrens of Marin and Lake Counties, California. Johnson, Pearson, and Stout (202) used a similar California soil in rating a variety of crops with regard to their sensitivity to molybdenum deficiency. Preliminary greenhouse studies have been conducted on soils of Oregon[8] and Maine[9] with alfalfa as the test crop. Soils of southern and western Oregon were found to respond to molybdenum at a pH of 5.3 or less; in Maine three out of nine soils gave significant response at pH 5.0 to 5.5. The three Maine soils that responded were derived from parent materials showing calcareous influence. Alfalfa responded to molybdenum at pH 5.5 in New Jersey on Norton silt loam derived from Triassic shale (120). Kretchmer (216) in Florida observed some

[2] H. M. Reisenauer, personal communication.
[3] C. L. Shrewsbury, personal communication.
[4] M. E. Marvel and C. B. Sperow, personal communication.
[5] F. C. Stark, personal communication.
[6] R. L. Winklepleck, personal communication.
[7] C. B. Sayre, personal communication.
[8] R. K. Kirsch, personal communication.
[9] C. S. Brown, personal communication.

benefit from molybdenum on white clover growing on acid Immokalee fine sand. Lettuce responded to molybdenum at reactions below pH 6 on five out of six uncultivated Connecticut soils (303). Two of the soils were derived from calcareous parent materials. Soybeans on two acid North Carolina soils, Loyd clay loam and Norfolk sandy loam, gave greater yields and higher nitrogen content when treated with molybdenum.[10]

SOIL FACTORS IN MOLYBDENUM DEFICIENCY

Kline (210) and Purvis (288) recently reviewed the relationships between the availability of molybdenum and soil reaction, aeration, and levels of manganese, phosphate, and sulfate. Molybdenum deficiency is often associated with acid soils because molybdenum becomes less soluble as the pH falls. Most of the occurrences reported in this review (table 1) fall into this category. Adjustment of the soil pH with lime, which releases soluble molybdenum to the soil solution, thus becomes an important method of overcoming molybdenum deficiency.

Well-limed or naturally neutral soils may also be depleted of available molybdenum by cropping or by leaching (120, 202). The molybdenum-deficient serpentine soils studied by Walker (353) and by Johnson *et al.* (202), and the limestone-derived soils of Sussex County, New Jersey, on which alfalfa responded to molybdenum (119), fall into this category. Surface horizons of many soils derived from calcareous parent materials in the humid regons are acid, and crops on some of these soils have been found to respond to molybdenum in New York (289) Connecticut (303), and Maine.[11] These soils were possibly depleted of available molybdenum by a less acid leaching milieu in the earlier stages of development and thus might be expected to be more deficient in molybdenum than are neighboring soils on acidic parent materials.

A number of surveys have been made of the total molybdenum content of soils of the United States.[12] Robinson and Alexander (298) have remarked upon the small variation in total molybdenum content of most soils. A few workers have measured the solubility of soil molybdenum in various extracting solutions of different pH value (34, 120, 144). Barshad (34) noted that a relation seemed to exist between water-soluble molybdenum and the molybdenum content of certain plants growing on soils with pH values between 4.7 and 7.5. Robinson and Edgington (299) found that, in general, the most fertile soils furnish the most available molybdenum to the plant, but their data indicate little or no relationship between total soil molybdenum and molybdenum availability. Walker[13] has assayed the available molybdenum of some California, Oregon, and Washington soils by the *Aspergillus niger* method. He reported that serpentine soils are much lower in available molybdenum than are nonserpentine soils, and that acid residual soils are lower than acid alluvial or glacial soils.

[10] H. J. Evans, personal communication.
[11] C. S. Brown, personal communication.
[12] References 32, 119, 287, 299.
[13] R. B. Walker, personal communication.

EXTENT OF MOLYBDENUM DEFICIENCY IN THE UNITED STATES

Because much of the evidence is fragmentary, it would be hazardous to estimate the extent of molybdenum deficiency in the United States. In several states not mentioned in this report, research on the subject was started only recently, and in states that have already reported deficiencies further instances will undoubtedly be uncovered.

The experiences with molybdenum deficiency on the acid sandy soils of Florida, New Jersey, and Long Island would appear to make all similar soils of the Atlantic and Gulf coasts suspect for certain crops, but these soils can be considered deficient only at a given pH, since liming releases adequate molybdenum to the crop.

Soils that respond to molybdenum at neutral or alkaline reactions can be considered truly deficient in this element. Such soils do exist in the United States, but their extent is unknown. Molybdenum-deficient acid soils of the humid regions that developed from calcareous parent materials may occupy an intermediate position, for although they respond to lime, they may have lost more available molybdenum during their development than have soils from more acidic parent materials.

Many relationships between molybdenum and soil factors other than pH have been studied, but almost no evidence is available on their applicability to deficiencies in the United States.

MOLYBDENUM TOXICITY

Although this paper is primarily concerned with molybdenum deficiency, brief mention of molybdenum excess is pertinent. Some soils of the United States have been found to be very high in total molybdenum, and vegetation growing on them has been found to be toxic to cattle. Barshad (32, 34, 35) studied various factors governing the uptake of molybdenum by plants growing on the high-molybdenum soils of the San Joaquin Valley, California. Excess molybdenum in pasture forage has been noted in lowland areas near the mouth of the Columbia River in Oregon and in some mountain meadows of central and southern Oregon.[14] Excess molybdenum also occurs in forage grown in mucks and peats of the Everglades in Florida (145, 216). In a greenhouse study, Robinson *et al.* (297) found that heavy applications of lime on a soil high in total molybdenum (DeKalb silt loam from Bloom, Virginia) produced legumes the molybdenum content of which exceeded the lower toxic limit for cattle. Gammon *et al.* (144) have expressed concern over the possible danger to livestock of the liming and conversion to pasture of molybdenum-treated fields.

SUMMARY

Field deficiencies of molybdenum have been reported in 13 states and are suspected to occur in three others. The crops most commonly involved have been

[14] R. K. Kirsch, personal communication.

alfalfa, cauliflower, and citrus, but other affected crops include broccoli, tomato, cantaloupe, lettuce, sweet potato, sweet clover, and peas. Greenhouse experiments have shown deficiencies in four states that have not yet found deficiencies in the field.

Evidence available at present suggests that the soils most likely to be deficient in the United States are the acid sandy soils of the Atlantic and Gulf coasts. Some deficiencies have also occurred on well-limed or naturally neutral soils and on acid soils derived from calcareous parent materials.

Excess molybdenum has been found in California, Oregon, and Florida soils.

ROLE OF MOLYBDENUM IN PLANT NUTRITION

HAROLD J. EVANS

North Carolina State College, University of North Carolina[1]

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The biological importance of molybdenum was not realized until 1930, when Bortels (47) showed that the element was highly beneficial in the fixation of gaseous nitrogen by *Azotobacter chroococcum*. This organism grew very poorly in a culture medium lacking combined nitrogen unless traces of molybdenum were supplied. The experiments of Bortels, which have been confirmed and supplemented by many other workers (41, 189, 247), indicated that molybdenum is indispensable for the fixation of nitrogen by a variety of Azotobacter species. Bortels' (49) observations also gave the first indication of the role of molybdenum in the fixation process by leguminous plants. Pea, soybean, and red clover plants grown in sand cultures showed striking increases in nitrogen fixation and growth from the addition of traces of molybdenum or vanadium to the culture solutions. Since this original discovery, a host of accumulated evidence[2] shows conclusively that molybdenum is essential for the fixation of nitrogen by bacteria growing symbiotically with legumes. The wide occurrence of molybdenum deficiency in legumes grown in certain soils of Australia was first pointed out by A. J. Anderson.[3]

That a physiological role of molybdenum in nitrogen fixation is not limited to Azotobacter, and symbiotic leguminous bacteria was indicated by Jensen's (196) observations that certain species of Clostridium require this element when grown without combined nitrogen. Experiments of Bortels (50), Fogg (137), and Wolfe (389) also provide strong evidence that molybdenum is required for the fixation of nitrogen by *Anabaena cylindrica*.

The first evidence of a physiological role of molybdenum not associated with nitrogen fixation was provided by the work of Steinberg (319, 320) initially reported in 1936. When *Aspergillus niger* was grown on media containing nitrate nitrogen and no added molybdenum, yields of mycelia were reduced by 96 per cent. In contrast, the decrease in yields of dry matter of the fungus resulting from the lack of molybdenum was only 4 per cent when cultured on media containing ammonium nitrogen. Steinberg suggested that the reduced molybdenum requirement for Azotobacter when combined nitrogen was substituted for gaseous nitrogen, and the reduced requirement for *A. niger* when ammonium nitrogen was utilized instead of nitrate nitrogen, had a common basic significance. That molybdenum is essential for the utilization of nitrate by *A. niger* has been adequately confirmed by Mulder (247) and Nicholas *et al.* (259).

[1] Contribution from the Division of Biological Sciences, North Carolina Agricultural Experiment Station, paper 688. Some of the work at North Carolina State College reported in this paper was supported by a grant from the Climax Molybdenum Co.

[2] References 117, 194, 197, 247.

[3] Reported by Anderson elsewhere in this issue.

Steinberg's discovery undoubtedly stimulated investigations concerning the possibility that molybdenum is essential for growth of higher plants. In 1939 Arnon and Stout (28) produced molybdenum-deficient tomato plants in six successive experiments conducted under rigidly controlled conditions. Piper (273) in 1940 described molybdenum-deficiency symptoms in oats and reported that 0.02 ppm. of the element in nutrient solutions was adequate for normal growth. Since the original demonstration that molybdenum is essential for tomato plants, cultural and nutrient purification methods have been developed which have enabled many investigators[4] to show that molybdenum is indispensable for a variety of plant species. A list of these plants includes cauliflower, cabbage, mustard, alsike clover, red clover, lucerne, pea, bean, rye, barley, cocksfoot, swede, sugar beet, flax, celery, radish, carrot, potato (165, 167, 173), citrus plants (344), and tobacco (321). The work of Evans *et al.* (117) and Meagher *et al.* (237) indicated that leguminous plants require molybdenum when grown on either atmospheric or nitrate nitrogen. With nitrate nitrogen as the source the requirement is, however, less than that for fixation.

It is generally agreed that higher plants are similar to *A. niger* in that they require considerably greater quantities of molybdenum for the utilization of nitrate than for the utilization of more reduced compounds such as ammonia or urea (2, 344). Nitrates accumulate in the tissues of a molybdenum-deficient plant and the protein content of the plant is reduced (117, 247). It follows, therefore, that in plant metabolism one role of molybdenum is either directly or indirectly associated with nitrate reduction. Since it has been clearly shown (2, 344) that certain plant species, including citrus and cauliflower, require molybdenum when grown on sources of nitrogen other than nitrate, and that a deficiency of the element results in profound chemical changes in tissues apparently not associated with nitrate metabolism, molybdenum is obviously involved in biochemical processes of nonleguminous plants other than nitrate reduction. Some of the experimental evidence necessary for the interpretation of the biochemical role of molybdenum in plant metabolism is considered in the following sections of this paper. Since recent literature concerning the relation of molybdenum to plant nutrition has been reviewed in detail by various authors,[5] no attempt has been made to include herein all references to work concerning the role of this element.

ROLE IN NITROGEN FIXATION

Reviews by Wilson (373, 382) and Mulder (247) have indicated that molybdenum is the one mineral element which is specifically and consistently associated with the mechanism of nitrogen fixation. Molybdenum, as noted, is involved in nitrate reduction. Since there may be common pathways in the assimilation of both nitrate and fixed gaseous nitrogen, it might be argued that molybdenum is involved in a common step in the assimilation of each of these nitrogen sources. But clear demonstrations (117, 237, 389) that both leguminous plants and algae

[4] References 117, 165, 167, 237, 321.

[5] References 115, 173, 229, 247, 277.

require greater quantities of molybdenum for utilization of gaseous nitrogen than for utilization of nitrate greatly weaken this argument.

Elucidation of the biochemical role of molybdenum in the process of nitrogen fixation obviously cannot precede understanding of the biochemistry of the nitrogen fixation mechanism per se. The nature of the latter process for the most part still remains obscure (381, 382). As a result of the research of P. W. Wilson, R. H. Burris, and their co-workers (381, 382, 383), however, facts recently have been uncovered which not only are possibly related to the nitrogen-fixation mechanism but also may involve a role of molybdenum in the process.

Some of the earlier work that led to these new findings includes the observation that molecular H_2 inhibited nitrogen fixation in Azotobacter, Nostoc, and red clover (383). An analysis of the nature of the inhibition indicated that H_2 competed with N_2 for some active site on the surface of an enzyme involved in fixation. It was also established that Azotobacter (222), certain Clostridium species (310), and *Rhodospirillum rubrum*, (147), all of which fix N_2, contain an enzyme which specifically activates H_2 [reaction (*1*)].

$$H_2 \rightleftarrows 2H^+ + 2e \qquad (1)$$

A peculiar characteristic of the hydrogenase enzyme is its nonspecificity for oxidant. The electrons may be transferred from H_2 to dyes, cytochrome *c*, nitrate, pyridine nucleotides, oxygen, or ferricyanide (311, 379). That hydrogenase was in some manner associated with nitrogen fixation by Azotobacter was suggested when the appearance of the enzyme was found (222) adaptive to N_2 rather than to H_2. An association of hydrogenase of *R. rubrum* with nitrogen fixation was suggested when experiments demonstrated that the photochemical evolution of H_2 by the organism was inhibited by N_2 (147). Presumably the H_2 was oxidized by enzyme-bound N_2 or a derivative of it. This observation led to the establishment of the capacity of this organism to fix gaseous nitrogen.

Even though nitrogen fixation by red clover is inhibited by H_2, all efforts to identify a hydrogenase in the nodules of legumes have failed (380). It seems logical to assume, therefore, that if hydrogenase is associated with nitrogen fixation in organisms such as *Azotobacter* sp., *Clostridium pasteurianum*, and *R. rubrum*, and if there is biochemical unity in the fixation mechanism in general, then some other enzyme analogous to hydrogenase participates in the symbiotic system. A possible relation of hydrogenase to nitrogen fixation according to Koffler and Wilson (212) is that nitrogen gas adsorbed by nitrogenase is reduced by the hydrogenase system. The alternate adsorption of nitrogen gas and water on the nitrogenase surface results in an initial oxidized product which is then reduced by electrons via the hydrogenase system.

The possibility that hydrogenase is indeed associated with the nitrogen fixation mechanism in *C. pasteurianum* and *Azotobacter vinelandii* has been greatly strengthened by recent experiments of Shug *et al.* (310, 311). Hydrogenase from cell-free extracts of the former organism have been partly purified and characterized. The enzyme has been shown to be a flavoprotein which specifically requires flavin-adenine dinucleotide as a prosthetic group. Dialyzed preparations

lost their capacity to reduce cytochrome *c* or nitrate, and activity was restored by addition of MoO_3. These workers further demonstrated that the absorption spectrum of the hydrogenase enzyme shows characteristic peaks depending on the gaseous phase in contact with the enzyme preparation. If the enzyme is reduced by admission of 0.2 atmosphere of H_2 (0.8 atmosphere of vacuum) and an absorption spectrum plotted, a characteristic curve is obtained. When 0.8 atmosphere of O_2-free N_2 is admitted to the cuvette, a change in the spectrum is noted with peaks at 405 and 425 mμ in the Soret region. This has been interpreted to indicate that N_2, chemisorbed upon the nitrogenase enzyme, oxidizes the reduced molybdoflavoprotein (hydrogenase), resulting in the observed spectral characteristics. If the ratio of H_2 to N_2 in contact with the enzyme is great (that is, 0.8 atmosphere to 0.2 atmosphere, respectively), then the hydrogenase remains reduced and this, in turn, presumably results in an inhibition of fixation by H_2. Shug *et al.* (311) have suggested that their experiments may prove to be a spectral demonstration of the nitrogen fixing system. In this writer's opinion, these experiments are of great significance in the elucidation of the mechanics of the fixation process.

Since tests for the presence of hydrogenase in the nodules of leguminous plants have consistently produced negative results, Shug *et al.* (311) have issued a note of warning concerning the assumption that this enzyme is intimately associated with nitrogenase in the fixation mechanism in general. The possibility that enzymes other than hydrogenase are associated with nitrogenase in nodules of legumes in a manner analogous to that proposed for hydrogenase and nitrogenase in Clostridium and Azotobacter (311) is discussed in another section of this paper.

MOLYBDENUM AND NITRATE REDUCTION

The degree of nitrate accumulation in the tissues of molybdenum-deficient plants is indicated in table 1[6]; similar results have been reported by a number of other investigators.[7] In this particular experiment[6] cantaloupe plants grown on Norfolk sandy loam with a pH of 5.2 developed a severe chlorosis of the lamina and a necrosis of leaf edges. The dry leaves of deficient plants contained a mean of 5880 ppm. nitrate nitrogen; spraying with a solution of sodium molybdate resulted in decrease of nitrate nitrogen to a normal level and recovery from the chlorosis. Recently Spencer and Wood (316) produced strong evidence that molybdenum is specifically involved in the conversion of nitrate to nitrite rather than in the transformation of other nitrogen metabolites involved in steps preceding protein synthesis. They treated molybdenum-deficient tomato plants with molybdenum and followed the changes in leaf content of nitrate, nitrite, ammonia, amides, amino acids, and proteins. Two days after treatment they found a striking decrease in concentration of nitrate and a marked increase in ammonia, amides, amino acids, and proteins. Within 4 hours, the nitrite and ammonia content of leaves was doubled. Wolfe's (390) experiments with

[6] Unpublished experiments of Harold J. Evans, North Carolina Agricultural Experiment Station, 1951.

[7] References 117, 169, 247, 384, 385.

TABLE 1

*Effect of molybdenum deficiency on accumulation of nitrate in cantaloupe plants grown on Norfolk sandy loam in North Carolina**

Description of Leaves	Date Sampled	Nitrate N in Dry Leaves†
		ppm.
Normal	August 2, 1951	900
Deficient	August 2, 1951	5880
Normal	August 10, 1951	743
Deficient	August 10, 1951	3965
Deficient, sprayed with Mo‡ August 2, 1951	August 10, 1951	1040

* Unpublished experiments of Harold J. Evans, North Carolina Agricultural Experiment Station, 1951.

† Means of determinations from four replicate plots. L.S.D. (0.01) = 854.

‡ Sprayed with 0.1 per cent solution of Na_2MoO_4.

Anabaena cylindrica suggest that molybdenum is indirectly involved in nitrate reduction by this organism. It is difficult if not impossible, however, to establish the site of action of an element without the isolation and characterization of the enzymes concerned with the metabolic processes in question.

It has been established[8] that both soybean and alfalfa plants possess a high endogenous capacity to reduce nitrate to nitrite, but in the experiments no reproducible differences between deficient and normal tissues were obtained. These negative results can now be reconciled by the fact that at the time the experiments were conducted (1948–1950) the nature of action of the nitrate reductase enzyme was not understood. In 1952 experiments[9] were initiated to test the hypothesis that reduced pyridine nucleotides are the natural electron donors for nitrate reduction. The first positive results were obtained with extracts from soybean leaves, but *Neurospora crassa* proved to be a better source of the enzyme (121). Approximately a 75-fold purification of enzymes from both soybean leaves and *N. crassa* (122, 254) resulted from these experiments. The enzymes catalyze the oxidation of reduced diphosphopyridine or triphosphopyridine nucleotides (DPNH or TPNH) by nitrate to yield the corresponding oxidized nucleotides and nitrite. The reaction catalyzed for the soybean enzyme is as follows:

$$\text{DPNH or TPNH} + H^+ + NO_3^- \rightarrow \text{DPN}^+ \text{ or TPN}^+ + NO_2^- + H_2O \qquad (2)$$

Enzymes from both soybean leaves and *N. crassa* proved to be flavoproteins with flavin-adenine dinucleotide as the natural prosthetic group. The enzymes from the two sources are not identical, as shown by the high specificity of the Neurospora enzyme for TPNH and differences in pH optimums for maximum activity.

[8] The writer in conjunction with Dr. E. R. Purvis and Dr. F. E. Bear became interested in the enzymatic process of nitrate reduction while studying (1948–1950) the molybdenum nutrition of alfalfa at Rutgers University.

[9] By the writer in conjunction with Dr. Alvin Nason at The Johns Hopkins University.

A metal constituent of both enzymes was suggested by the strong inhibition of activity by NaN_3, KCN, and other chelating agents.

The first evidence that molybdenum is associated with the nitrate reductase was provided by Nicholas *et al.* (259). When either *N. crassa* or *A. niger* was grown on highly purified media without added molybdenum a striking reduction in nitrate reductase activity of extracts of the fungal mycelia was noted. Activity of deficient cultures was restored to normal level 12 hours after molybdenum was added to them. Other metals added did not evidence a similar capacity. These studies also indicated that molybdenum deficiency resulted in a decreased glutamic dehydrogenase activity of extracts.

More convincing evidence that molybdenum is indeed a part of the Neurospora nitrate reductase is the demonstration of Nicholas and Nason (260) that dialysis against KCN and glutathione deactivates the enzyme but incubation of the dialyzed enzyme with either MoO_3 or Na_2MoO_4 restores its activity. These workers also showed that a correlation exists between the molybdenum content, expressed on a protein basis of fractions of enzyme preparations of different purities, and the specific enzyme activities of the fractions.[10]

Recently Nicholas and Nason (258) in a study of the mechanism of the Neurospora nitrate reductase reaction, established the order of the reduction sequence to be:

$$\text{TPNH} \rightarrow \text{FAD or FMN} \rightarrow \text{Mo} \rightarrow NO_3^- \qquad (3)$$

That reduction of flavin-adenine dinucleotide (FAD) or flavin mononucleotide (FMN) precedes reduction of molybdenum was shown by the fact that the molybdenum-free enzyme lost its capacity to reduce nitrate by either TPNH or reduced flavin. The metal-free enzyme, however, will catalyze the reduction of FAD or FMN by TPNH. Addition of molybdenum specifically restored the capacity of the enzyme to catalyze the reduction of nitrate. These investigators also provided evidence that chemically reduced molybdate (probably pentavalent molybdenum) enzymatically reduced nitrate to nitrite in a reaction mixture lacking TPNH and FAD or FMN.

Molybdenum is also a constituent of the soybean leaf nitrate reductase, as indicated in experiments by Evans (123), Evans and Hall (125), and Nicholas and Nason (262). Evans and Hall treated young soybean seedlings with a solution containing Mo99 and 6 days later harvested the leaves and prepared cell-free extracts for enzyme fractionation. The results of a typical experiment (table 2) show a close correlation between enzyme activity and radioactivity of the fractions of highest purity. Similar evidence came from Nicholas and Nason (262), who determined by a biological assay method the molybdenum content of various fractions containing the enzyme. Dialysis of the soybean leaf reductase by the methods described by Nicholas and Nason (260) removed the endogenous molybdenum and resulted in a decrease in enzyme activity (125, 262). The capacity

[10] The key to the success of these experiments undoubtedly is associated with the skill of Dr. D. J. D. Nicholas in dealing with traces of molybdenum from the standpoints of purification and analytical procedures.

TABLE 2

Association of radio molybdenum with nitrate reductase during purification (125)*

	Fraction	Protein	Enzyme Activity†	Radio-activity
		mg./ml.	*units‡*	*counts/sec.‡*
I	Crude extract	3.00	9.4	8.9
II	First gel eluate	0.38	189.2	10.5
III	0–50% $(NH_4)_2SO_4$ precipitate	0.52	368.0	12.7
IIIA	Supernatant from III	0.34	6.4	5.0
IV	Second gel eluate	0.19	1006.6	30.0
IVA	Residue after second gel adsorption	0.20	8.0	6.0

* The purification procedure was identical with that described previously by Evans and Nason (122) except that a 0–50 per cent $(NH_4)_2SO_4$ precipitate was obtained in fraction III instead of a 0–40 per cent precipitate.

† One unit of enzyme activity is defined as that amount required to produce 1×10^{-3} μM of nitrite in 5 minutes using the standard assay (122).

‡ Expressed per milligram of protein.

TABLE 3

Effect of metals on reactivation of cyanide-dialyzed nitrate reductase (262)

Treatment	Units of Enzyme Activity/0.2 ml. Enzyme	
	Experiment I	Experiment II
I. Undialyzed enzyme	7.3	7.1
II. Single dialysis*	6.0	5.2
III. II + cyanide ($10^{-3}M$)	0	1.6
IV. Successive dialysis†	0	1.0
Added metals:		
MoO_3	—	6.2
Na_2MoO_4	—	5.8
$FeCl_3$	—	1.2
$FeSO_4$	—	1.3
$ZnSO_4$	—	1.0
$MnSO_4$	—	1.0
$CoSO_4$	—	1.3
$NiCl_2$	—	1.2
AgCl	—	1.0
$NaWO_4$	—	1.5
$Na_2Cr_2O_7$	—	1.1
Na_3VO_4	—	1.5
$VO_2(NO_3)_2$	—	1.5
$Na_2B_2O_4$	—	1.0

Note: Enzyme assay as described under "Materials and Methods" (262).

* Dialyzed for 3 hours against 0.1 M phosphate $+10^{-3}M$ glutathione. All reagents were freed from Molybdenum as indicated.

† As for treatment III, followed by redialysis for 2 hours as in treatment II. Protein content of 0.2 ml. enzyme, 107 μg.; 1 μg. of each metal added to 0.2 ml. of enzyme and incubated for 10 minutes at room temperature before enzyme assay.

to reduce nitrate was specifically restored by addition of MoO_3 or $NaMoO_4$ (table 3). Though the enzyme must be dialyzed at pH values of 7.0 or above to remove molybdenum, samples of enzyme dialyzed against KCN and glutathione at a pH value below 7.0 showed small but consistent stimulation from addition of Fe salts (125). Nicholas and Nason (262) established that electrons are transferred from reduced pyridine nucleotide to flavin to molybdenum and then to nitrate, a sequence which is identical with that established for the Neurospora reductase. In 1955 Nicholas and Nason (261) described a pyridine nucleotide nitrate reductase from *Escherichia coli* with molybdenum and flavin requirements analogous to those described from Neurospora and soybean.

In 1954 Evans (124) reported that the nodules from a variety of leguminous plants contained an enzyme which catalyzed the reduction of nitrate to nitrite. Cell-free extracts of *Rhizobium japonicum* isolated from soybean nodules are highly specific for reduced diphosphopyridine nucleotide as an electron donor for the reaction. The nodule enzyme is different, therefore, from that in Neurospora or soybean leaves. The nitrate reductases from the various sources, however, are similarly inhibited by NaN_3, KCN, and copper and manganese salts. The nodule reductase, which is extremely labile, is associated with particulate matter in cells, and the direct demonstration of possible metal or flavin cofactor requirements has, therefore, been complicated. Laboratory experiments[11] have succeeded in purifying the nodule enzyme some 15- to 20-fold and have established that the kinetics differ entirely from those reported for other nitrate reductases. An association of molybdenum with the enzyme is indicated by the fact that molybdenum deficiency in soybean plants results in a striking decrease in the enzyme activity in nodules.

Although it was thought that the nitrate reductase in nodules was probably involved in the metabolism of nitrates that entered nodules either from soils or from impurities in mineral salts supplied to plants grown in sand cultures, recent experiments (66)[12] have provided evidence that the activity of the reductase in nodules is associated with nitrogen fixation rather than an external supply of nitrate to cultures. Since the synthesis of nitrate reductase in pure cultures of *Rh. japonicum* requires nitrate in the media, it is adaptive to this form of nitrogen (66), although, perhaps significantly, under these conditions no nitrogen is fixed. On the other hand, sterile soybean plants, inoculated with pure cultures of *Rh. japonicum* and cultured aseptically with a nutrient solution lacking combined nitrogen, contain relatively high nitrate reductase in nodules. One must conclude, therefore, that in the process of nitrogen fixation by soybean plants, nitrate or some other substance induces the adaptive formation of nitrate reductase. It is inviting to speculate that chemisorbed N_2 upon the nitrogenase enzyme or an oxidized product resulting from this chemisorption may induce the adaptive formation of nitrate reductase in nodules. If this compound is something other than nitrate, it can be assumed that the nodule reductase is nonspecific for oxidant and therefore analogous to hydrogenase, which will catalyze the reduc-

[11] Unpublished experiments by George Cheniae, North Carolina State College.

[12] Including unpublished experiments by George Cheniae.

tion of many compounds including nitrate. Possibly DPNH-nitrate reductase in soybean nodules may play a role in nitrogen fixation analogous to that proposed for the molybdoflavoprotein hydrogenase in other nitrogen fixing organisms. Experiments now in progress will, it is hoped, determine whether DPNH-nitrate reductase in soybean nodules is a true nitrate reductase involved in the metabolism of nitrate derived from initial products of fixation (possibly a side reaction during fixation) or whether this enzyme is nonspecific for oxidant and concerned with the reduction of products other than nitrate that may or may not be involved in fixation.

RELATION TO OTHER METABOLIC PROCESSES

Molybdenum undoubtedly plays a vital role in plant metabolism other than that associated with nitrate reduction and nitrogen fixation. Agarwala (2) demonstrated that cauliflower plants grown with various nitrogen sources, including urea and ammonium sulfate, developed characteristic molybdenum deficiency symptoms known as "whiptail" and contained reduced concentrations of ascorbic acid. Vanslow and Datta (344) provided evidence that the lemon plant requires molybdenum when grown on nitrogen entirely in the ammonium form. In general, the role of molybdenum in plant processes not associated with nitrate reduction is poorly defined.

Hewitt (173) pointed out that reduced concentration of ascorbic acid in tissues is a characteristic of molybdenum deficiency in a number of species, and Evans *et al.* (117) indicated that molybdenum-deficient alfalfa leaves have a lower capacity to reduce methylene blue than do normal leaves. Similar observations by Hewitt and Agarwala (183) showed that molybdenum deficiency in a variety of plant species results in a reduced capacity to catalyze the reduction of triphenyltetrazolium chloride. A relationship between molybdenum deficiency and dye reduction would suggest a role in electron transport. What the possible significance of these observations is, however, will have to await further investigation. Millikan (241, 243*a*) reported that excesses of a series of heavy metal cations interfere with the normal utilization of iron by flax. These toxic effects can be alleviated under certain conditions by addition of molybdenum to cultures. Similar observations have been made by the writer,[13] but the nature of any mechanism whereby molybdenum is involved in iron metabolism remains obscure. The beneficial effect of a complex of molybdate with ferrous sulfate as compared to ferrous sulfate alone in the treatment of certain types of anemia in humans is of interest in this regard (164).

Possingham (286) grew molybdenum-deficient tomato plants, treated them with the deficient element, and during their recovery observed changes in organic and inorganic phosphorus. Plants receiving molybdenum exhibited a greater capacity to convert accumulated inorganic phosphorus into organic phosphorus than did those lacking this element. Spencer (315) pointed out that molybdate is a powerful competitive inhibitor of the acid phosphatases from the tomato plant and suggested that the concentration of this element normally found

[13] Unpublished experiments.

in plants is of sufficient magnitude for metabolic significance in the inhibition of phosphatase reactions. It seems reasonable to postulate that excessive phosphatase activity in tissues resulting from molybdenum deficiency would deplete the normal level of phosphorylated metabolites and therefore indirectly affect the synthesis of ascorbic acid.

Recent experiments by Westerfeld and Reichert (373), DeRenzo *et al.* (90), Totter *et al.* (336), Mackler *et al.* (230), and Kielley (208) showed that xanthine oxidase from either cow's milk or rat liver is a flavoprotein containing both iron and molybdenum. Xanthine oxidase catalyzes the oxidation of hypoxanthine, xanthine, reduced pyridine nucleotide, or aldehyde by oxygen, cytochrome c, nitrate, or certain dyes. To the writer's knowledge there is no evidence of the occurrence of this enzyme in higher plants. Aldehyde oxidase, which is a flavoprotein similar to xanthine oxidase, except that it is highly specific for the oxidation of aldehydes, has been purified from pig's liver by Mahler *et al.* (233). Both molybdenum and hematin iron are associated with the purified enzyme. There is evidence that higher plants contain an enzyme that catalyzes the oxidation of aldehydes, but no metal or other cofactor requirements have been established for it. Perhaps the demonstration of both molybdenum and iron as metal cofactors for certain enzymes will provide a clue to an elucidation of the *in vivo* molybdenum-iron interaction (241).

SUMMARY

From a review of the role of molybdenum in plant metabolism, it is concluded that molybdenum is an essential element in the process of nitrogen fixation, and in nitrate reduction in plants when this source of nitrogen is utilized. It is, however, not a role which is limited to these two physiological processes, for plants grown upon combined nitrogen sources other than nitrate still require molybdenum for normal growth. The magnitude of the molybdenum requirement for nitrogen fixation and nitrate reduction is greater than that for the utilization of the reduced combined nitrogen sources.

There is evidence in the literature that hydrogenase is intimately associated with the nitrogen-fixation mechanism in certain free-living nitrogen-fixing microorganisms. Molybdenum has been shown to be an essential constituent of this enzyme. The possibility that a molybdoflavoprotein similar to hydrogenase plays a role in nitrogen fixation by symbiotic bacteria analogous to that proposed for hydrogenase in certain free-living microorganisms has been discussed.

It is concluded that there is convincing evidence that molybdenum functions as an electron carrier in the flavoprotein-nitrate reductases recently isolated from soybean leaves, Neurospora, and *Escherichia coli*. This adequately accounts for the accumulation of nitrate in tissues of plants that are deficient in molybdenum.

There is strong evidence that molybdenum may play a role in the inhibition of plant phosphatases. But the relation of this element to ascorbic acid accumulation and diminished capacity for dye reduction, and to iron metabolism, all of which have been associated with deficiency of the element, remains obscure.

Central Florida Expt Sta

HIBISCUS . . . Although it is best known in vegetable and field crops, molybdenum deficiency also occurs in ornamentals such as roses, carnations, sunflowers, marigolds, and hibiscus. In "strap-leaf" of hibiscus, shown here, the affected leaves though dark green are stunted and constricted laterally and have prominent distorted, parallel veins.

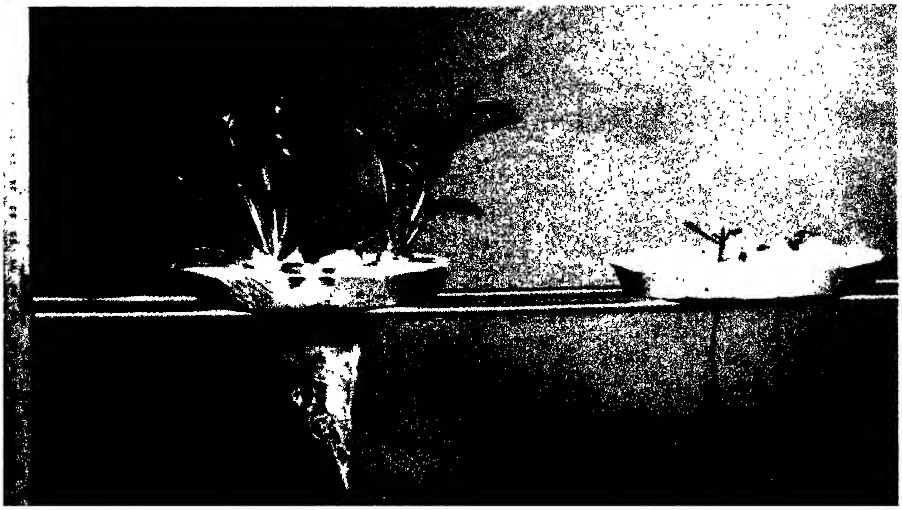
MOLYBDENUM DEFICIENCY

symptoms in crops

Molybdenum performs two essential functions in plants. It is required in all crops for the reduction of nitrates to ammonia as the first step in protein synthesis. In legumes it is also required for nitrogen fixation.

Molybdenum-deficient plants show characteristic symptoms. In legumes these are the well-known signs of nitrogen starvation — pale yellow foliage, stunted growth, and patchiness in the field. Most other crops have poor, irregular growth and an overall pale yellowish cast. In many species pronounced chlorotic areas develop between the leaf veins. In severe cases tissue in these areas dies. Some broad-leaved plants such as cucumber and cantaloupe show marked marginal chlorosis.

Leaf distortions are common. Margins often curl or "cup" upwards around the rim. In cauliflower and some other crucifers leaf tissue develops irregularly from the midrib to produce long narrow leaves. This disease, "whiptail," is the most specific indication of molybdenum deficiency.

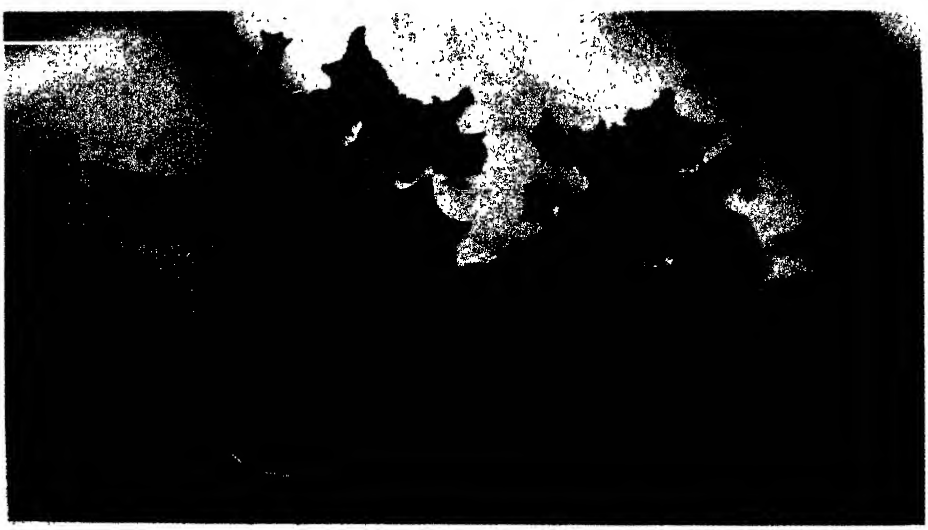


California Agr. Expt. Sta.

SUGAR BEET . . . The effect of molybdenum deficiency on growth varies greatly. Crucifers, beets, spinach, tomatoes, lettuce, and small-seeded legumes are most strongly affected. Note the extreme effects on the growth of both roots and tops in these sugar beets.

ICE . . . Overall pale yellowish color or chlorosis is characteristic of nearly all molybdenum-deficient crops. Note the color difference in these lettuce plants between the normal plant on the left and the deficient plant on the right. Note also difference in growth.

Univ. of Connecticut Storrs Agr. Expt. Sta.

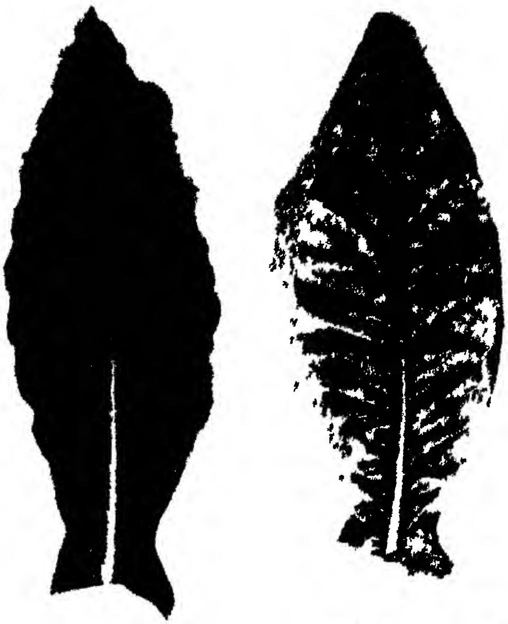


Queensland Dept Agr & Stock

BEANS... The chlorosis is nearly always localized between the veins, as in these bean plants. Since nitrogen was supplied, the beans here were functioning as a nonlegume. After spray treatment with sodium molybdate, a nearby row turned green within a few days.

GRAPEFRUIT... In citrus the chlorotic areas appear as clearly defined spots, and the deficiency is therefore called "yellow spot." Affected areas of the leaf become brown and gummy and eventually die. Trees gradually lose their leaves and produce little fruit.

Florida Citrus Expt Sta



New Jersey Agr Expt Sta

New Jersey Agr Expt Sta

TOBACCO . In many plants the contrast between the darker veins and the lighter interveinal areas gives the whole leaf a mottled effect Chemical tests show a high concentration of unreduced nitrate in the chlorotic spots

CAULIFLOWER . . . Whiptail of cauliflower is the most striking and specific symptom of molybdenum deficiency Leaf tissue develops irregularly from the midrib to produce long, narrow leaves Often the leaf edges are contorted or pleated in appearance.

Rhode Island Agr Expt Sta

In severe cases of whiptail, heads are often unmarketable or fail to develop altogether Usually only the younger leaves are whiptailed. Older leaves appear normal in mature plants, but are chlorotic between the veins during the earlier stages of growth

. A curling inwards or "cupping" of the leaf margin is a common deficiency symptom In broccoli and cauliflower it occurs temporarily in the first leaves before symptoms of whiptail appear In other crops it persists in all leaves throughout growth

California Agr Expt Sta

Univ of Bristol Agr & Hort Res Sta Long Ashton

TOMATO The characteristic cupping or curling in of the leaf margin is less noticeable in small-leaved plants such as tomatoes, but is still an important symptom to observe Note also the marked yellow mottling between the veins and the death of the growing tip

CUCUMBER In pumpkins, squash, cantaloupe, melons, and similar crops with flat broad leaves, chlorosis and cupping may occur in a narrow band around the margin Note the up-curled rims and dead tissue around the outer edges of these deficient cucumber leaves

Queensland Dept Agr & Stock

New Zealand Dept. Agr.

WHITE CLOVER . . . Legumes need more molybdenum for nitrogen fixation than for conversion of nitrates to protein. Accordingly, molybdenum deficiency shows primarily as yellowing, stunting, and general unthriftiness — all very characteristic of nitrogen starvation.

RED CLOVER . . . In severe cases, some symptoms of true molybdenum deficiency, such as incurled leaves and marginal scorch, appear in legumes. Note the change from a healthy, normal condition to progressive stages of deficiency in these leaves of red clover.

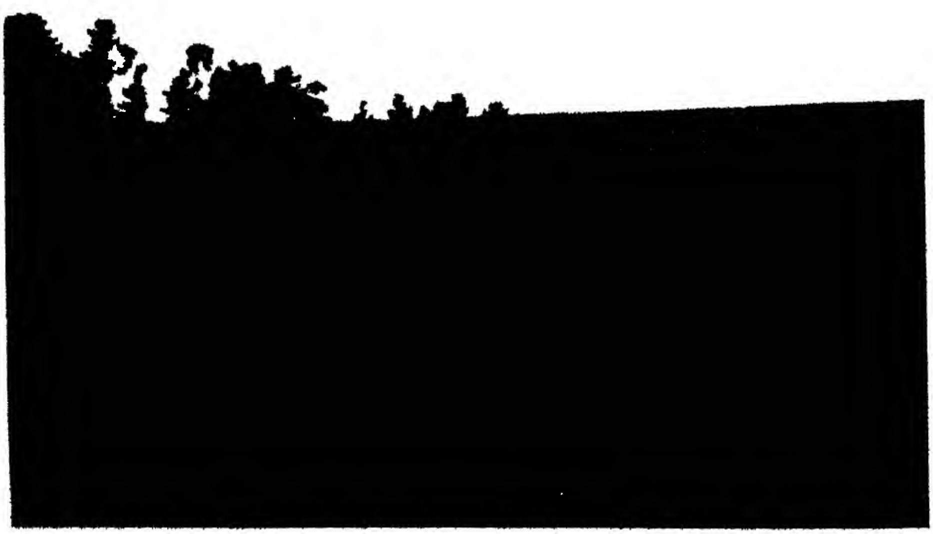
Univ. of Bristol Agr. & Hort. Res. Sta., Long Ashton

Climax Molybdenum Co

ɫ.ALɫ 4 . . . Both sides of this alfalfa field in New Zealand were sprayed with molybdenum salts. In the untreated center area the crop is pale yellow and stunted. Growth is poor and irregular, with occasional healthy green patches scattered through the area.

rr AA T . . . Molybdenum deficiency often occurs irregularly throughout a field, probably because of variations in soil acidity or composition. This wheat field in New Zealand shows an unusual contrast between healthy (dark) and deficient (pale yellow) areas.

Climax Molybdenum Co



FACTORS AFFECTING MOLYBDENUM AVAILABILITY IN SOILS

E. B. DAVIES

Rukuhia Soil Research Station[1]

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It was a striking coincidence that within a space of 2 years discoveries were published of the harmful effects of molybdenum excess (128) on the one hand, and on the other, of molybdenum deficiency (8) the one affecting stock, the other pasture. These initial findings led to the identification of widely scattered occurrences of both phenomena. The present article discusses these incidences and the soil factors with which they are associated.[2]

TOTAL MOLYBDENUM IN SOILS AND ROCKS

The average content of molybdenum in the lithosphere has been reported by Rankama and Sahama (290, p. 39) as 2.5–15 g./ton (ppm.), by Goldschmidt (149, p. 74) as 2.3 ppm., and by Kuroda and Sandell (218) as 1.0 ppm. Kuroda and Sandell pointed out a uniformity of molybdenum distribution due largely to its ability to replace a number of other elements of similar ionic radius in the lattices of rock-forming minerals. Robinson and Alexander (298) from a consideration of their own very numerous results and other published data, suggested an average of 2.3 ppm. in soils. Fifty-seven determinations by Wells (370) representative of New Zealand soils averaged 2.3 ppm., whereas Grigg's results[3] gave a slightly lower mean. Kidson's (207) analyses of soils in the Nelson province of New Zealand gave the particularly low mean of about 0.6 ppm. Vinogradov and Vinogradova (346) published the molybdenum contents of profile samples representative of the zonal soils of the U.S.S.R. ranging from tundra soils within the Arctic Circle to red loams in the far south. Results fell into the narrow range of 2–4 ppm. with one exception—12 ppm. in the A_0 to A_1 horizon of a mountain tundra. Except at very low levels, the total molybdenum content of soils, however, cannot be considered a guide to available supplies, for deficiencies have been observed in particularly well supplied soils (ironstone soils, for example).

CRITERIA OF AVAILABILITY

Striking abnormalities in availability of molybdenum first became known through research into the cause of "teartness in Somerset" (128); research on responses of clover in unsatisfactory South Australian pasture to wood ash (8); and research on "whiptail" of cauliflowers in New Zealand (80, 244). The characteristic symptoms of molybdenum excess in animals and molybdenum deficiency in plants still help to point out extremes. Yield trials including

[1] Department of Agriculture, New Zealand.

[2] The author is indebted to Mr. N. Wells and to Messrs. M. Fieldes and K. I. Williamson for the opportunity of reading their papers in manuscript.

[3] Unpublished data.

molybdenum treatments show more precisely the adequacy of molybdenum supply to *Rhizobia* or higher plants under the conditions obtaining. Possible complexities are well shown in the studies of Mulder (252) and Walker, Adams and Orchiston (356).

Herbage content

Determination of the molybdenum content of herbage will show whether the levels are likely to be toxic to stock, and has also been used as an indication of availability to the plant. Robinson and Edgington (299) determined the molybdenum content of a variety of plants on some 24 soils and calculated the "available" molybdenum on the basis of an arbitrary crop of 2 tons from 2 million pounds of soil per acre. The molybdenum content of plants varies with the species and the age and part of plant, factors which have to be taken into account. Wells (369) studied the nutrient status of some 220 New Zealand soil types for 25 elements through analysis of sweet vernal (*Anthoxanthum odoratum*) taken at the same point of growth, the flowering period (his results in respect to molybdenum will be referred to later).

The molybdenum content of legumes can be a poor guide to adequacy of supply, for normally a deficiency limits growth through restricting symbiotic nitrogen fixation. Anderson and Oertel (10) commented on this. Walsh, Neenan, and O'Moore (357) reported the high values of 2 ppm. molybdenum in subterranean clover and 2.5 ppm. in white clover on molybdenum-responsive soils. Molybdenum tends to concentrate in the nodules (193, 247). In results reported by Walker, Adams, and Orchiston (356) the molybdenum content of clover tops was frequently lower in plants treated with molybdenum even though a yield response was recorded. In *Brassica* studies, Plant (279) mentioned the complicating effect of manganese. Nevertheless, in nonlegumes, more especially those not susceptible to manganese toxicity, molybdenum content of selected material, as in the work of Wells, should give a useful indication.

A preliminary trial of Davies (85) with sodium tungstate on permanent pasture gave some indication that tungsten could act in place of molybdenum, presumably in nitrogen fixation by *Rhizobia*. Any such effect could complicate the correlation of analytical and yield results.

Bioassay

Mulder (247) and Nicholas and Fielding (257) have assessed available molybdenum by the growth of *Aspergillus niger*. Mulder (252) made use of the fact that

TABLE 1

Bioassay of trace elements from Australian soils (107)

Soils	Number Examined	Very Deficient	Deficient	Slightly Deficient
Surface soils	278	—	2	5
Subsoils	164	3	—	6

A. niger is not subject to certain interactions to the same extent as are higher plants. Donald, Passey, and Swaby (107) studied the use of a number of microorganisms in the determination of trace metals and eventually used *A. niger* (Mulder's strain) in a survey of 278 surface soils and 164 subsoils from eastern Australasia. They point out, however, a number of disadvantages in the method among which are: the production by the *Aspergillus* of large amounts of organic acid capable of liberating trace elements from soil minerals; the fact that the organism obtains most of its trace elements via solution rather than contact exchange; that it is insensitive to wide variations in the superoptimal concentration of all microelements except copper; and that a large percentage of soils inhibit growth of *A. niger*. Their results with molybdenum are summarized in table 1. The oxalate method applied by Grigg (156) to five of these soils gave results of the same order.

Chemical methods

A variety of extractants have been used in attempts to assess available molybdenum, for example, neutral normal ammonium acetate (245, 143), normal ammonium acetate adjusted to pH 9 with NH_4OH (36), 1.0 N NH_4OH (144), and water (32, 34, 324). Gammon *et al.* (144) extracted Rutledge fine sand with a range of solvents from 10 N HNO_3 to 10 N NH_4OH. The alkaline and 10 N acid solutions extracted the most molybdenum, the 0.1 N HNO_3 the least.

The only method extensively checked against field trials and used in advisory work employs an ammonium oxalate extractant (155), following the formula of Tamm of pH 3.3. The oxalate ion is held to exchange with MoO_4^{--}, which complexes with excess oxalate. The single extraction in consequence is considered to remove all exchangeable molybdenum. The response level of pastures (and it is the clover constituent which responds) was found to be about 0.14 ppm. Grigg (155) noted a connection with pH, responses in general not occurring above pH 6.3. Later, as the number of field trials increased, Davies (82) found that a fair prediction of response could be made if interpretation was modified according to pH. At pH 5 the response level was 0.20 ppm.; at pH 6.5, 0.05 ppm. Lucerne had a higher requirement. The complicating factor of manganese antagonism is probably implicated to some extent in this need for considering reaction. Walker, Adams, and Orchiston (355), in trials on six Canterbury (New Zealand) soils, found no relationship between molybdenum content of clovers and grasses on their sulfate-plus-phosphate plots and the "available" molybdenum determined by this method, nor could the results be explained in terms of pH. The various interactions mentioned elsewhere weigh against a close connection between "available" molybdenum and molybdenum uptake or response. This method, nevertheless, proved very useful in the first identification of deficient areas (81). Walsh, Neenan, and O'Moore (357) found that, where molybdenum excess was present in herbage, the oxalate method gave figures in the range 0.20–0.70 ppm., whereas deficient soils varied from 0.04–0.12 ppm.

INSTANCES OF MOLYBDENUM EXCESS AND DEFICIENCY

In the following discussion, pasture or crop responses are taken as the indication of molybdenum deficiency, and stock trouble or herbage high in molybdenum content as that of excess.

Excess

The excessive molybdenum levels in herbage in Somerset (224) and in Kern County, California (59, 32) [and presumably in the wider incidences reported by Goss (151)] are associated with alkaline soils, in the first case with unusually high amounts of total molybdenum. Walsh, Neenan, and O'Moore (357) reported excesses on mineral soils quite normal in total molybdenum content (0.5–3.5 ppm.) but of neutral to alkaline reaction, and also on organic soils of the cutaway bog type, particularly those of high calcium status, underlain by calcareous marl. The condition was favored by high phosphate status. They (358) describe a further case on an acid soil of pH about 5.0 with remarkably high oxalate-soluble molybdenum, 0.80–0.90 ppm. In this instance the phosphate was low and the soil presented no features commonly associated with toxic herbage. Cunningham, Brown, and Edie (72) gave no soil details of the Swan River valley incidence with pastures containing up to 25.6 ppm. Mo.

In New Zealand, Cunningham (78) has surveyed pastures of both islands for copper and molybdenum content. Pastures were collected in spring, the period of maximum molybdenum level, from all the main soil types. He listed those likely to produce herbage of molybdenum content above normal. Grigg and associates[4] analyzed by the oxalate method soil samples drawn at the time of collection. Of the soils producing pasture of more than 5 ppm. Mo content, some are alkaline of marine origin (Ahuriri clay loam, Meeane-Farndon complex) but the majority are acid with a pH range of 5.3–6.4. The pH of one soil was as low as 4.6. These acid soils comprise certain recent alluvial soils, skeletal soils derived from mudstone and sandstone, yellow-gray earths[5] from mudstone, and notably yellow-brown soils derived from volcanic ash (Taupo shower) in the Wairoa area. Elsewhere Taupo ash soils do not give rise to trouble. In the Wairoa soils the oxalate figures average slightly more than 0.40 ppm. molybdenum.

Peats were not included in the soil results under discussion. Cunningham (73) showed medium-high levels of molybdenum in peat pastures, which in combination with subnormal copper contents give rise to the stock ailment "peat scours." He also demonstrated a dangerous rise in the pasture molybdenum induced by quite low applications, and expressed concern as to the probable concentration of molybdenum in the soil as the peat mineralizes and consolidates (76).

[4] Unpublished data.

[5] For the relationship of N. H. Taylor's provisional genetic classification of New Zealand soils with systems in the U.S.A. and Great Britain, *see New Zealand Dept. Sci. Ind. Research Soil Bur. Bull.* (n.s.) 5: 275. 1953.

Deficiency

Europe. Mulder (252) reported molybdenum deficiency in soils rich in ironstone and organic matter and in acid sandy soils (249) in Holland. Vinogradova and Drobkov (347) obtained a marked response of clover on a "clover tired" soil, but the level of molybdenum in the control plants (1.7 ppm.) was high enough to suggest that the trouble was not simple molybdenum deficiency. Plant (281) in England found occurrence of whiptail on a wide range of acid soils derived from granite, Devonian (shale), Old Red Sandstone, and Keuper and Lower greensand. The first report of whiptail in England (268) was on a soil containing calcium carbonate. Walsh, Neenan, and O'Moore (357) in Eire obtained a response of subterranean clover on a sandy soil (pH 5.3) and of white clover on an organic soil (pH 5.5). Again the molybdenum content, 2.0 and 2.5 ppm., respectively, mentioned earlier, was high for deficiency.

United States. Incidences of molybdenum deficiency in the United States are considered elsewhere in these papers. Suffice it here to note that most occur in the eastern states. In the West an interesting case of molybdenum deficiency was reported by Walker (353), who recognized deficiency symptoms in tomatoes on the "serpentine barren" soils in Lake and Marin Counties in California. The pH (soil paste) values were relatively high, 6.3–6.8. Johnson, Pearson, and Stout (202) reasoned that the near neutral and sometimes alkaline reaction of the soils minimizes anion adsorption and favors losses of molybdate, phosphate, and sulfate by leaching. Fourteen serpentine soils examined were low in molybdenum-supplying power.

Australia. In Australia, the earliest evidence of molybdenum deficiency, afforded through responses of subterranean clover and lucerne (8), was rapidly followed by Fricke's work (138, 139) with Cressy shaley clay loam in Tasmania and pot trials by Ferres and Trumble (131) in South Australia. Later, whiptail gave the clue to widely scattered instances in Queensland, New South Wales, Victoria, and West Australia. Hudson and Cradock (191) mapped deficient areas in New South Wales; Mullett (253) detailed numerous occurrences in Victoria; and Trumble and Ferres (338) found through pot and field experiments instances from the southeast border of South Australia to the Eyre peninsula. Dunne and Jones (109) listed West Australian areas subject to whiptail, and Dunne (110), Rossiter (302), and Teakle (334) mentioned other instances. Teakle laid down a series of 32 test strips with molybdenum treatment on ironstone gravelly soils distributed widely in Southwest Australia but in only one obtained a definite response. Carroll (64), in a study of the ancestry and mineralogy of the soils of Southwest Australia, remarked that the most widely distributed element seems to be molybdenum.

On the soil map of Australia[6] there is a great band of podzolic soils which stretches down the east coast from Queensland through New South Wales and Victoria to South Australia, and includes the larger part of Tasmania and Vic-

[6] See "The Australian Environment," p. 40. C.S.I.R.O., Melbourne, 1950.

toria. It is in this zone that most instances of molybdenum deficiency are found. Many of the soils are derived from lateritic remnants, others from quartzites, granites, shales, and slates. Graham (152) described soils of known and suspected molybdenum deficiency as being highly weathered with a high percentage of quartz and extremely low amounts of feldspars. A very low amount of ferromagnesium and ferrocalcium minerals was found in some of the samples. In general, molybdenum-deficient soils were characterized by a very small amount of minerals in the heavy fraction.

Stephens (323) drew particular attention to the areas of red loams associated with basalts and other more or less ferruginous rocks. On such acid soils, with pH often about 5, legumes respond to molybdenum. Stephens expressed little doubt that this response is due to the general unavailability of molybdenum in soils of high anion-exchange capacity when pH values are low.

A different type of occurrence is that recorded by Dunne and Jones (109) on alkaline soils, for example, orange colored "tuart" sands (pH up to 8.2) and calcareous loams at Coogee, which contain as much as 70 per cent $CaCO_3$ and have pH values up to 8.6. The deficiency may be due to the ready loss of MoO_4^{--} under alkaline conditions. Dunne and Jones also mentioned whiptail instaces on peaty swamp soils with pH 4.2–5.8.

New Zealand. In New Zealand molybdenum responses have been obtained from the extreme south to the far north (84). The largest area of highly responsive soils occurs in the South Island among the damp and wet coastal yellow-gray earths[5] of the Balclutha-Gore, Taieri, North Otago, and South Canterbury districts. These are soil types of the downs country of low original fertility (228) formed on loess of schist and graywacke origin. Warepa silt loam (328) and Opuha silt loam (227) are two of the soil types on which many spectacular responses have been obtained. Kauru silt loam, a soil derived from sandstone in North Otago, has also proved highly, if erratically, molybdenum-responsive. Lynch (228) referred to slight deficiencies on the more fertile downs country of North Otago and Canterbury (the dry coastal yellow-gray earths), soils derived from graywacke loess and alluvium. Marked results from molybdenum applications have been obtained on Marlborough Sounds hill soils, in the Nelson district where Kidson (207) showed particularly low figures for total molybdenum, and recently on "pakihi," a glei podzol soil in West Nelson (65*b*, 111).

In the North Island, pasture responses have been recorded on hill soils derived from graywacke from Wellington to the Manawatu, and in the Auckland province on soils from sandstone, graywacke, andesitic, and doleritic rocks. Basalt soils are discussed later.

No responses have been recorded on yellow-brown soils derived from rhyolite and rhyolitic pumice in the central plateau of the North Island or from yellow-brown loams from fine andesitic ash.

Though in New Zealand molybdenum deficiency is associated with parent material to some extent, the key to the scattered incidences lies rather in the soil-forming factors of weathering and leaching, for much of the rock is of similar composition. This is discussed later.

FORMS OF COMBINATION

For discussion purposes, forms of molybdenum may be classified under the following four heads:

Unavailable (held within the crystal lattice of primary and secondary minerals)

Conditionally available (retained as the MoO_4 anion by clay minerals and available to a greater or less degree depending on pH and probably phosphate status)

In organic matter

Water-soluble

Unavailable molybdenum

Most soil molybdenum, amounting in the comparative analyses of total and oxalate-soluble molybdenum in New Zealand soils by Grigg (155) and Kidson (207), to some 90 per cent, is in this resistant fraction. Grigg drew attention to an instance in which of a total of 0.94 ppm. molybdenum but 0.10 ppm. could be extracted with boiling HCl. The particular soil was a mature podzol consisting largely of silica sand. The molybdenum in ironstone gravels would be included under this general heading.

The basalt-derived red and brown loams of North Auckland, New Zealand, provide an interesting example of how in the course of weathering molybdenum may be released from the primary mineral to a more available state, only to be once more trapped at a later stage. In the immature stage these soils contain, as their clay, amorphous hydrous oxides of aluminum, iron, and titanium; at the semimature stage, fine particle size crystalline gibbsite, boehmite, and goethite, and anatase occur with the amorphous hydrous oxides; in the mature stage, crystalline oxides preponderate, with a small amount of kaolin and minor amounts of amorphous material (132). At the first stage, the soil has a high anion-exchange capacity and molybdate derived from the basalt is held in exchangeable form. With age the hydrous iron oxides crystallize, and the molybdenum becomes occluded and again unavailable (370).

Bell (39) recorded a lack of molybdenum response on the immature basalt soils of North Auckland (Kiripaka and Ohaeawai loams), slight responses on the semimature soils (Ruatangata clay loam), and more positive responses on the mature ironstone soils (Okaihau gravelly clay loam). Molybdenum retained by amorphous hydrous oxides is extractable by the oxalate reagent, and the following analyses by Grigg[7] show the wide difference between levels in young and mature soils:

Soils	Stage	Total Mo, *ppm.*	"Available" Mo, *ppm.*
Whatatiri clay loam..................	Young to immature	4.6	1.11
Okaihau gravelly friable clay..........	Submature to mature	6.7	0.07

[7] Private communication.

Anderson and Oertel (10) pointed out that good pastures have been observed on lateritic peneplain soils and suggested that weathering of the ironstone *in situ* may release sufficient molybdenum for normal growth. The relationship between iron compounds and molybdenum availability will be discussed further.

Conditionally available (or exchangeable) molybdate

A connection between soil reaction and molybdenum availability (see later) has been extensively reported, and Stephens and Oertel (322) early suggested that the effect could be due to an anion exchange of the type $MoO_4 \rightleftarrows OH$ and and mentioned as an analogy the favorable effect on phosphate supply of raising the pH. Stout *et al.* (330) have shown that tomatoes take up molybdenum far more readily from acid culture solutions. The effect of raising the soil pH must, therefore, be sufficiently potent in releasing molybdate ions to more than counterbalance the inhibiting effect on uptake. Stout *et al.* (330) showed that MoO_4^{--} was "fixed" by hydrated halloysite and that much could be released by moderately alkaline solutions. Goldberg found molybdenum fixation to increase with acidity down to pH 2.2, and all such molybdenum fixed by exchange could be released by alkaline solutions of pH 9 (330). Barshad (34) found halloysite, kaolinite, and clay colloids in general to absorb relatively large amounts of molybdenum from solutions up to pH 7.5, the pH rising during the process; no molybdenum was absorbed above pH 7.5. Davies (83) observed that MoO_4^{--} was progressively absorbed from solution by soils with accompanying release of phosphate. Oxalate also belongs to this group of more or less mutually exchangeable anions (219), and Grigg's extractant already described would presumably remove the molybdenum considered in this section. There seems little doubt that molybdate is held as an exchangeable anion, that appreciable proportions of soil molybdenum may be in this form, and that soil reaction has a marked effect on its availability.

Molybdenum in organic matter

Plants tend to act as accumulators of molybdenum. Ter Meulen, for example, (238) has reported 1.12 ppm. Mo in *Azolla* growing in canal water containing only 0.00009 ppm. Mo. Barshad (34) has suggested intensive cropping as the best method of reducing soil molybdenum where pasture levels are toxic to stock. Robinson and Edgington (299) calculated the theoretical numbers of crops needed to exhaust various soils of molybdenum. Goldschmidt (149, p. 559) mentioned a concentration of molybdenum in certain coal ashes and in forest litter. The molybdenum in peats has already been mentioned. Barshad (34) presented data which show an increase in water-soluble molybdenum with ignition; Grigg (155) noted a correlation between loss on ignition of soils and molybdenum extracted by 2 per cent NaOH and suggested a definite fraction of molybdenum as being associated with the soil organic matter. Gammon *et al.* (144) extracted Florida "flatwoods" soils with 1.0 N NH_4OH, as they considered that in the fine sands concerned most molybdenum would be in organic form. Of profile analyses available to the writer, only that on the Kola peninsula re-

ported by Vinogradov and Vinogradova (346) shows a surface concentration that might be associated with organic matter.

There is a paucity of data on the molybdenum content of organic matter in soils. It is likely to be in a continual state of circulation through microbial breakdown.

Water-soluble molybdenum

Water-soluble molybdenum would normally be very low. Only under alkaline conditions, such as instances reported by Barshad (34), would the fraction assume any magnitude.

FACTORS AFFECTING MOLYBDENUM NUTRITION OF PLANTS

The molybdenum status of soils has been judged to a considerable extent by the response of plants to applications. It is important to recognize the modifying effects of soil reaction and of interactions with other elements. Stout *et al.* (330); Johnson, Pearson, and Stout (202); Mulder (252); and Walker, Adams, and Orchiston (355, 356)—all have made detailed investigations.

Soil reaction

There is wide experience that heavy liming and molybdenum application frequently bring about the same improvement in yield. That liming increases the availability of soil molybdenum is supported by the following selected examples. The molybdenum-deficiency disease "whiptail" was countered by liming (67, 232) long before the true nature of the disease had been demonstrated. Plant (279, 281) showed that 5 tons of crushed limestone per acre, found when analyzed to contain negligible amounts of molybdenum, and 4 pounds of ammonium molybdate were equally effective in controlling whiptail; both treatments, moreover, raised the molybdenum levels of cauliflower leaves to the same degree. Though lime and molybdenum treatments both reduced the manganese content of leaves, Plant, presumably from visual evidence and the manganese levels in the cauliflowers, considered that in his experiments manganese toxicity was not a complicating factor. Mulder (252) using *A. niger*, which is said to be unaffected by manganese, showed molybdenum in soils to be more available with the medium at pH 6.8 than at pH 5 or pH 2. Evans, Purvis, and Bear (120), extracting Nixon loam with normal ammonium acetate solutions adjusted to cover a pH range of 5.0 to 9.5, removed increasing amounts of molybdenum with rise in acidity. Piper and Beckwith (276) demonstrated the greatly increased uptake both of native and applied molybdenum from two red-brown earths by *Medicago denticulata*, *Erodium cygnorum*, and *Hordeum leporinum* at higher reactions. Oertel, Prescott, and Stephens (267) studied by pot experiment the growth of subterranean clover in Cressey shaley clay loam adjusted to pH values ranging from 3 to 10. In presence of added molybdenum (corresponding to roughly 1 pound sodium molybdate per acre), yields rose rapidly at pH 4.5 and attained a maximum from pH 5.8 to 7.9. Without molybdenum, equal maximum yields were obtained, but only over the range pH 6.9–7.9.

In New Zealand, negative interactions of lime and molybdenum were clearly shown in early pasture trials at the Invermay Research Station and in a Southland trial (81).

Evidence of the critical effect of pH on molybdenum uptake at the toxicity level is afforded by Lewis's work (224) on the "teart" soils of Somerset. If the pH was below 7 pasture was nontoxic, even though the soil might contain as much as 33 ppm. total molybdenum.

Interactions

Stout *et al.* (330) showed phosphate to greatly increase subterranean clover uptake of both native and added molybdenum, but in a subsequent crop of garden peas a similar result was not apparent. An anion exchange effect is possible, but it was noted that molybdenum uptake of tomatoes grown in water culture was similarly enhanced, the major influence possibly being on the translocation of molybdenum from the roots to the tops (330, 329). Mulder (252) presented data which demonstrate that above a certain basal requirement the response of *A. niger* to molybdenum is independent of the phosphorus supply, and he used the *Aspergillus* method to demonstrate increases in available molybdenum in soils due to phosphate additions. He pointed out that on molybdenum-deficient soils, the need for phosphate could be reduced through molybdenum application.

The sulfate ion exerts a depressing action on molybdenum uptake (330, 252), an effect attributed by Stout *et al.* (330) to competition of similarly sized and charged ions. On an alkaline soil Barshad (35) obtained no such effects. Superphosphate (in New Zealand) contains roughly 50 per cent calcium sulfate. The respective influences of the phosphate and sulfate on molybdenum availability would tend to offset each other. Manganese-molybdenum antagonism in plant nutrition is important[8] and undoubtedly a factor confusing any attempt to assess the molybdenum status of soils from plant uptake (356). Wells (370) found a moderate negative correlation between the molybdenum and manganese contents of sweet vernal.

Trumble and Ferres (338) noted frequent positive interactions of potassium and molybdenum in pot experimental work. Rossiter (302) noted a strong interaction of molybdenum and potassium in absence of lime in an experiment with *Trifolium subterraneum* L. on a coarse siliceous sand. Barshad (35) demonstrated a reduction in molybdenum uptake of *Lotus corniculatus* and *Trifolium repens* (var. *Latum*) by ammonium, but was working with a soil of unusually high molybdenum-supplying power. The NH_4^+, SO_4^{--}, and increased acidity may all have contributed to the favorable action of ammonium sulfate observed by Lewis (225) in reducing molybdenum content of toxic pasture. Warington (368) has reviewed recent work on molybdenum and micronutrient interactions.

[8] References 15, 22, 243, 252.

WEATHERING AND LEACHING

In the discussion under forms of combination, reference was made to molybdate as an exchangeable anion on clay minerals. Fieldes and Swindale (132) and Fieldes and Williamson (133) in examining the clay minerals of New Zealand soils showed the frequency of amorphous hydrous oxides of iron and aluminum. Wells (370) in a study of molybdate-ion fixation in New Zealand soils considered these amorphous hydrous oxides responsible for molybdate "retention." He assessed retentive capacity by shaking soils with a molybdate solution and determining the percentage of molybdenum going to the soil phase. Molybdenum availability was gaged on the molybdenum content of sweet vernal (*Anthoxanthum odoratum*), a grass of wide distribution, sampled at the flowering stage. Wells applied these measures of molybdenum retention, "plant molybdenum," and also total molybdenum in the topsoil to sequences of soils derived from similar parent materials, thus seeking to trace the changes in molybdenum status during the course of soil development. His general thesis is that the retentivity is associated with the amount of amorphous hydrous oxides, that this amount is low in lightly weathered soils and increases with weathering, and that concomitantly the molybdenum becomes less available. In mature soil, for example, the basalt-derived Okaihau gravelly clay loam already mentioned, the amorphous hydrous oxides are held to have crystallized—as Fieldes and Swindale found through electron micrography—"fixing" the molybdenum in the crystal lattice. With strong podzolization iron and aluminum are lost from the topsoil. In consequence, the remnant of molybdenum is more available and "plant molybdenum" higher. Eventually an absolute deficiency would develop.

On this basis one would expect high levels of "plant molybdenum" in young soils, decreasing levels as weathering progressed, a slight rise in mature podzols, and low values as absolute deficiency was approached. In the various sequences given by way of illustration some exceptions are apparent.

The total molybdenum content of soils has been shown to increase up to the semimature stage, but analyses of Grigg[9] of North Auckland soil suites do not bear this out in that they show a decrease in total molybdenum over the same phase of development.

Wells's ideas, however, do fit very neatly the pattern of responses observed on graywacke soils and permit a rational explanation of the varying incidences of molybdenum deficiency on soils derived from a common rock.

His concept of molybdenum availability is tied almost wholly to the nature of the iron compounds in the soil. Williams and Moore (376) found that the molybdenum uptake of Algerian oats in their experiments could be expressed in terms of pH and iron soluble in HCl by a regression equation of the form:

$$\text{Log } 100 \text{ Mo} = a \text{ pH} - b \text{ Fe} + c$$

All coefficients were significant at the 0.1 per cent level. The authors suggested that the availability of molybdenum may depend on that of the MoO_4 ion

[9] Private communication.

through an adsorption process by free iron oxides. The suggestion lines up closely with those of Wells. Robinson and Edgington (299) also have suggested a connection between abundance of free hydrated iron oxides and molybdenum availability, and the possibility of iron concretions' locking up molybdenum in an entirely unavailable form. Oertel and Prescott (266) earlier discussed such a mechanism of molybdenum fixation. Apart from allophane, clay minerals other than the amorphous hydrous oxides of iron and aluminum are not mentioned by Wells. There would seem to be possibilities of MoO_4^{--} retention by, for example, the metahalloysite, shown to be present in moderately and strongly weathered yellow-brown earths (132).

The strong influence of soil reaction on molybdenum availability was emphasized earlier. It could well determine the availability of the molybdenum in the highly retentive soils.

Wells considers that if the molybdenum content of sweet vernal is less than 0.5 ppm., pasture responses can be expected. If the low level is associated with a high capacity of the soil for molybdenum retention, then phosphate, lime, or vanadate application may release MoO_4^{--} and a response to applied molybdenum not be forthcoming.

SUMMARY OF CONDITIONS FOR MOLYBDENUM EXCESS AND DEFICIENCY

The following soils are prone to produce herbage of high molybdenum content:

Alkaline soils.

Organic soils [not all, for molybdenum deficiency has been noted on peats in West Australia (109), Eire (358), west coast of Norway (313), and New Zealand].

Some "young" soils [the sweet vernal samples of highest molybdenum content recorded by Wells (6.5 and 4.9 ppm.) both came from soils derived from recent volcanic showers; Cunningham's list of soils prone to give high-molybdenum pastures contained several skeletal hill soils derived from mudstone and sandstones (78)].

A general comparison of the pasture analyses of Cunningham (78) and corresponding soil figures for oxalate-soluble molybdenum makes it plain that factors other than those considered in this review must play a part in molybdenum uptake. Several acid pumice soils low in oxalate-soluble molybdenum and low in available phosphate (Truog) have produced pasture above normal in molybdenum content. Conversely, others, particularly high in oxalate-soluble molybdenum, only slightly acid, and more than adequately provided with phosphate have pasture levels below 1 ppm. A study of selected instances may throw some light on such anomalies.

The following soils are prone to be deficient in molybdenum:

Absolute deficiencies. These may occur on highly podzolized soils, a likely example being the soil at Houghton, Mt. Lofty, described by Anderson and Oertel (10) as derived from sedimentary quartzitic material. Soils with little capacity for retaining molybdate may also come under this category, for ex-

ample, calcareous sands, "serpentine barrens." The soils from "Moutere gravels" and granites listed by Kidson (207) are very low in total molybdenum.

Soils of high anion-exchange capacity (molybdenum-retentive capacity—Wells) and low pH.

Ironstone soils in which the molybdenum has become difficultly available.

Soils depleted by exhaustive cropping: Such cropping may have been a contributing factor in North Otago (226) and in the Longford Cressy area in Tasmania, where cereals have been grown for 80 to 100 years (101). The development of molybdenum deficiency has been noted (152) in many areas in Australia after 10 years of soil improvement with nitrogen and superphosphate.

METHODS OF SOIL AND PLANT ANALYSES FOR MOLYBDENUM

E. R. PURVIS AND N. K. PETERSON

New Jersey Agricultural Experiment Station[1]

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Current interest in the role of molybdenum in plant nutrition has stimulated critical study of analytical procedures for the determination of this element in soils and plants by a number of investigators.[2] As a result, it is now possible to determine a fraction of a microgram of molybdenum with more than 95 per cent accuracy. Colorimetric procedures are almost universally employed, separated into two groups on the basis of the reagents used to produce the colored complex with molybdenum. For each group, procedures are similar to methods originally employed for the analysis of molybdenum in steels.

The older and more generally employed procedure is based on the colored complex produced by the reaction of molybdenum and an alkali thiocyanate in presence of a reducing agent. According to Dick and Bingley (92), this reaction was first observed by Braun in 1863.

In 1948, Piper and Beckworth (275) introduced a new method for the analysis of plant material for molybdenum, and Williams (377) modified the method to include soils. The procedure is based on the precipitation and extraction of a green-colored molybdenum-dithiol complex after removal of certain interfering ions from the test solution, a reaction first noted by Hamence (162) in 1940, although he apparently did not appreciate the degree of sensitivity possible.

Of the few methods proposed for determining available molybdenum in soils, that employed by Grigg (155) appears to offer the most promise. In this procedure, the soil is extracted with acid ammonium oxalate solution buffered at pH 3.3 and the molybdenum in the extracting solution determined.

An investigation of the molybdenum status of New Jersey crops and soils has been in progress at Rutgers University since 1947. Hundreds of analyses for molybdenum content have been run on soil and plant samples. The analytical procedures employed have undergone a number of changes as the result of refinements worked out in this and other laboratories. In a recent comparison of the thiocyanate and dithiol methods, the authors found the dithiol procedure too tedious and time-consuming for routine work. Because of the increased number of operations it requires, chances for error are greatly increased, a weakness, it is believed, that more than offsets the greater sensitivity of the method.

The purpose of this paper is to present in detail the methods employed in this laboratory for analysis of soils and plants for molybdenum content and the data supporting the accuracy of the procedures followed. An outline of the method

[1] Paper of the Journal Series, New Jersey Agricultural Experiment Station, Rutgers, The State University of New Jersey, New Brunswick, department of soils.

[2] References 92, 116, 157, 203, 234, 275, 317, 377.

of Grigg (119) for extracting available molybdenum in soils is included to bring it to the attention of American investigators.

PREPARATION OF SAMPLES FOR ANALYSIS

The molybdenum content of soils and plants will rarely exceed a few parts per million. The difficulties involved in solubilizing and retaining through a long analytical procedure such small amounts of an element are obvious. One of the analyst's major obstacles lies in digestion of the initial samples. Since relatively large amounts of reagents are required at this stage, it is important that they be as free as possible of molybdenum. Water and acids should normally be redistilled in glass before use. Where purification is impossible, chemicals of satisfactorily low molybdenum content should be used, and shifts to new batches of a reagent in the middle of a procedure should be avoided. A blank determination should be run with each batch of reagents and subtracted from all subsequent determinations.

Plant samples (116)

Weigh out a 2-g. sample of oven-dried, finely ground plant material and place in a tall 200-ml. beaker. Add 15 ml. of concentrated HNO_3; cover beaker with a watch glass and heat on a hot plate at low heat until solid material disappears. Add 2 ml. of 70 per cent perchloric acid and digest to dryness at low heat. This should require a minimum of 3 hours. Remove watch glass, add 5 ml. of concentrated HNO_3 and 1 ml. of 70 per cent perchloric acid, and evaporate to dryness, reducing heat to avoid spattering as residues approach dryness. Add 2 ml. of 30 per cent H_2O_2 and again bring to dryness. Cool, add approximately 70 ml. of distilled water, and heat to boiling for 1 minute. Add 10 ml. of concentrated HCl, filter, allow to cool, and make up to 100 ml.

Soil samples (119, 162)

Thoroughly mix 2 g. of finely ground soil with 10 g. of anhydrous Na_2CO_3 and place in a platinum crucible. Cover crucible, place in a muffle furnace, raise heat to 900–950° C., and maintain at this temperature for 15 minutes. Remove from furnace and rotate and tip crucible so that melt forms thin layer as it solidifies. Place crucible and cover in 400-ml. beaker, tip crucible on side, and add sufficient distilled water to just cover crucible. Let stand overnight. Remove crucible and cover with glass rod and rinse with distilled water. Slowly add 50 ml. of concentrated HCl, using small portions to dissolve any residues remaining in crucible. Place beaker on steam bath, evaporate to dryness, and bake until residue is dry.

Add 10 ml. of concentrated HCl and 40 ml. of distilled water; cover with watch glass and digest on steam bath for 15 minutes. Filter through a Büchner funnel and wash with hot water containing 5 ml. of concentrated HCl per liter. Wash until all yellow color is removed from silica residue. Place filtrate and washings in a 250-ml. beaker and evaporate on steam bath until residue is crystalline in appearance. Add 40 ml. of distilled water and 10 ml. of concentrated

HCl; return to steam bath untill residue is dissolved. Filter and wash with distilled water to 100-ml. volume.

Extraction of available molybdenum from soils (155)

Weigh out 25 g. of air-dry soil into a 500-ml. Erlenmeyer flask and add 250 ml. of acid ammonium oxalate solution (24.9 g. of ammonium oxalate and 12.605 g. of oxalic acid per liter, adjusted to pH 3.3). Shake flask in automatic shaker overnight. Filter, and evaporate 200 ml. of filtrate to dryness in 100-ml. Pyrex beaker. Heat beaker in muffle furnace at 450° C. for 4 hours to destroy organic materials. Take up residue in 10 ml. of distilled water, add 10 ml. of concentrated HCl, and filter. Wash with distilled water and make up to 100-ml. volume. This solution contains the extractable molybdenum from 20 g. of soil.

DETERMINATION OF MOLYBDENUM (275, 162)

Reagents

Stannous chloride. Dissolve 20 g. $SnCl_2$ in 20 ml. of concentrated HCl by heating below boiling point. Make up to 200 ml. with distilled water. Prepare fresh daily.

Ammonium thiocyanate. 10 per cent solution.

Ferric chloride. Dissolve 49 g. of $FeCl_2 \cdot 6H_2O$ in distilled water and make up to 1 liter.

Sodium nitrate. Dissolve 42.5 g. of $NaNO_3$ in distilled water and make up to 100 ml.

Isopropyl ether. Place reagent grade isopropyl ether in a glass-stoppered separatory funnel and add one tenth its volume of a mixture containing one third each of $SnCl_2$ and NH_4SCN solutions and one third distilled water. Shake thoroughly and separate. Prepare fresh daily.

Standard molybdenum solution. Dissolve 0.150 g. of C.P. MoO_3 in 10 ml. of 0.1 *N* NaOH and make slightly acid with HCl. Dilute with distilled water to 1 liter. Dilute 20 ml. of this solution to 1 liter. Solution now contains 2 ppm. molybdenum, or 2 μg. per milliliter.

Procedure

Transfer 100 ml. of test solutions (prepared by procedures described for preparation of samples for analysis) to a 150-ml. glass-stoppered separatory funnel. Add 1 ml. of $FeCl_3$ solution, 1 ml. of $NaNO_3$ solution, 5 ml. of NH_4SCN, and 5 ml. of $SnCl_2$, shaking thoroughly after each addition. *Addition of $FeCl_3$ should be omitted in the analysis of soil samples for total molybdenum.* Add 10 ml. of isopropyl ether and shake by hand 100 times. Allow ether to separate, and draw off aqueous phase. Deliver ether into a glass-stoppered container. Determine transmittance at 475 mμ on a standard photoelectric colorimeter. Subtract reading for blank determination and determine molybdenum content of test solution by reference to standard curve.

Standard curve is prepared by following foregoing procedure with six or more aliquots of standard molybdenum solution containing 0 to 20 μg. of the element.

Representative results

Representative results obtained by these procedures are presented in table 1, 2, 3, and 4. The duplicate determinations reported in tables 1 and 3 were run on samples digested or fused separately, and the differences between the two samples represent the sum of the errors of sampling and analysis. Duplicate determinations run on portions of the same digest or fusion show considerably less variation, indicating that most of the error lies in sampling. The satisfactory degree of recovery of added molybdenum (table 2) supports this. As is to be expected, the sampling error is greater in soil than in plant material.

The results for available molybdenum (table 4) were obtained by extracting the soils by the procedure of Grigg (155) and preparing the extracts for analysis as previously indicated for preparation of samples for analysis. Agreement between replicate samples was excellent. There appears to be little correlation, however, between the available molybdenum content of the soil and the total molybdenum content of soil or plant. Since so few samples were used, no conclusions can be drawn from the results. Although soils 5 and 6 fell within the range considered deficient by Grigg, alfalfa grown on these soils contained 1.93 and 1.57 ppm. of molybdenum.

Field tests with molybdenum on alfalfa have been conducted for a 2-year period at the six locations from which the soil and plant samples were taken.

TABLE 1

Comparison of duplicate determinations of Mo content of alfalfa

Sample No.	Molybdenum Determination		
	A	B	Average
	ppm.	*ppm.*	*ppm.*
1	0.65	0.68	0.66
2	0.58	0.58	0.58
3	0.23	0.23	0.23
4	0.83	0.85	0.84
5	1.93	1.93	1.93
6	1.65	1.50	1.57

TABLE 2

Recovery of molybdenum added to alfalfa samples

Sample No.	Molybdenum			
	In sample	Added	Determined	Recovery
	ppm.	*ppm.*	*ppm.*	%
1	0.66	2.0	2.56	96
2	0.58	2.0	2.48	96
3	0.23	2.0	2.13	95
4	0.84	2.0	2.64	93
5	1.93	2.0	3.73	95
6	1.57	2.0	3.57	100

TABLE 3

Comparison of duplicate determinations of Mo content of soils

Sample No.	Molybdenum Determination		
	A	B	Average
	ppm.	*ppm.*	*ppm.*
1	1.58	1.70	1.64
2	2.15	2.00	2.07
3	2.21	2.21	2.21
4	1.30	1.50	1.40

TABLE 4

*Comparison of Mo content of alfalfa and soil with available Mo content of soils**

Sample No.	Molybdenum		
	Plant	Total in soil	Available in soil
	ppm.	*ppm.*	*ppm.*
1	0.66	1.64	0.22
2	0.58	2.07	0.30
3	0.23	2.21	0.25
4	0.84	1.40	0.39
5	1.93	1.00	0.10
6	1.57	0.79	0.14

* Available Mo extracted by method of Grigg.

No response to applied molybdenum was obtained in any of these tests, although sample 3 contained considerably less molybdenum than is normally found to be sufficient for alfalfa in New Jersey.

Because of the practical importance of finding a satisfactory method for determining the available molybdenum content of soils, work is being continued with the Grigg and other procedures.

DISCUSSION

In recent years the thiocyanate method for the determination of total molybdenum in soils and plants has been subjected to critical study by several investigators.[3] The formation of an orange-colored molybdenum-thiocyanate complex is produced in HCl solution in presence of a reducing agent. The colored complex can be extracted in ether or other suitable solvents and its intensity determined with a colorimeter.

According to Barshad (33), presence of ferric or nitrate ions results in oxidation of molybdenum present in the acid solution in reduced form. Barshad suggests that presence of these ions may also prevent reduction of molybdenum below the quinquivalent form after addition of a reducing agent. Dick and Bingley (92) have presented evidence that iron enters into the colored complex in the ratio of one atom of iron for each atom of molybdenum. Since soils normally

[3] References 33, 92, 157, 295.

contain sufficient iron for this purpose, no addition of iron need be made in their analysis.

The reducing agent, stannous chloride, serves a dual role: it reduces the molybdenum to the quinquivalent form, the valency required in the molybdenum-thiocyanate complex, and also reduces the iron, thus eliminating color interference by the red ferric thiocyanate complex. Some soils may contain sufficient iron to require more stannous chloride than that which the procedure specifies to bring about complete reduction of the ferric thiocyanate.

The present reporters found isopropyl ether satisfactory as an extractant for the molybdenum-thiocyanate complex. A single extraction suffices with soil and plant samples of normal molybdenum content. Where above-normal amounts of the element are encountered, extraction with a second 10-ml. portion of ether is required. It is important that the ether be thoroughly shaken with the solution before the separation is made. Isoamyl alcohol (92), and a heavier-than-water mixture of isoamyl alcohol and carbon tetrachloride (203) are among the several extracting agents recommended by other workers.

SUMMARY

Methods for determining the molybdenum contents of soils and plants, and the available molybdenum content of soils, are discussed. Tested procedures are outlined for the fusion of soil samples and the digestion of plant samples, in preparation for analysis for total molybdenum content.

The method of Grigg (155) for extracting available molybdenum from soils is described. A modified thiocyanate procedure for determining molybdenum in soil and plant extracts is presented in detail; the reactions involved are discussed and data are presented in support of the accuracy of the procedures described.

MOLYBDENUM IN ANIMAL NUTRITION

A. T. DICK

Commonwealth Scientific and Industrial Research Organization[1]

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The first observations on molybdenum in relation to animal nutrition concerned the toxic effects of this element. In 1938, Ferguson *et al.* (126) reported that in certain restricted areas in Great Britain a cattle disease, known locally at "teart" and characterized by extremely severe diarrhea and loss of condition, was attributable to the high molybdenum content of the pastures on which the animals grazed. These investigators were able to produce a similar condition in cattle either by dosing the animals with a molybdenum salt by drench, or by raising the molybdenum content of a pasture by application of molybdenum as a topdressing. Similar toxic effects in cattle grazing on pastures of high molybdenum content (15 to 300 ppm. dry weight) have since been reported from America (32, 59), Canada (72), New Zealand (75), and Sweden (161).

A number of studies on the toxicity of molybdenum to monogastric animals have been made since then (31, 69), and the possibilities of molybdenum in various forms as an industrial hazard for the human subject were also examined by Fairhall *et al.* (99).

Although earlier studies failed to demonstrate that molybdenum was an element essential in animal nutrition, Teresi *et al.* (335) concluded that if the growing rat needed molybdenum at all, its daily requirements must be less than 0.5 μg.

More recently, however, molybdenum was found to be a cofactor of the flavoprotein enzyme, xanthine oxidase (89, 373). The xanthine oxidase activity of the small intestine of weanling rats on a molybdenum-deficient diet increased when a molybdenum salt was added to their diet. By assay of the tissues for xanthine oxidase activity de Renzo *et al.* (88) estimated the maximum molybdenum requirement of the rat as 0.2–0.3 μg. per day. Molybdenum was subsequently shown to be a nondialyzable component of the enzyme (161, 200, 217). But these findings do not constitute a clear demonstration that molybdenum is an essential element for animal nutrition. As Underwood (341) puts it, "...in none of the experiments so far reported has the depletion of liver or intestinal xanthine oxidase been accompanied by any detectable disability in the experimental rats, nor has the addition of molybdenum to the xanthine oxidase depleting diets resulted in any improvement in their growth or metabolism. Until such effects are produced molybdenum cannot be said to have been unequivocably established as an essential dietary item in this or any other species."

The discovery that xanthine oxidase is a molybdenum enzyme led to the suggestion that the xanthine calculi found in the kidneys of sheep in a restricted area in New Zealand may be the result of a deficiency of molybdenum in the

[1] Animal Health Research Laboratory, Parkville, Victoria, Australia.

diet (38). Although there is some support for this suggestion in the finding that the soils of the area are "very low in molybdenum," the picture is probably complicated by the low protein intake of the sheep there. Under Australian conditions, it is not uncommon for sheep to graze pastures of molybdenum content of 0.01 ppm. or less, but adequate in protein, without any difficulties arising from calculi.

On the other hand, it was demonstrated in 1945 (91) that the molybdenum in the diet of ruminant animals could exert a profound effect on their copper metabolism. When sheep grazed on pastures of very low molybdenum content (less than 0.1 ppm. dry weight), copper rapidly accumulated in their livers (60); this could result in chronic copper poisoning and subsequent death of the animal. Conversely, under certain conditions, when the diet contains about 5 ppm. molybdenum, sheep may develop a clinical copper deficiency (391).

The interrelationship of copper and molybdenum in animal metabolism has been the subject of a number of studies from which most of the current knowledge of molybdenum metabolism has been derived.

In both ruminant and monogastric animals, it has been shown that there is an antagonism between molybdenum and copper in their normal metabolism, and that the toxic effects of molybdenum can be prevented by increasing the copper intake. Little light has been thrown on the mechanism of this interaction, but there is a considerable body of evidence in studies on ruminants to show that not only molybdenum metabolism but also the interaction between copper and molybdenum is markedly affected by the inorganic sulfate content of the diet, and there are indications that other dietary factors may also be involved. In monograstric animals, Marston and Dewey[2] found the toxicity of molybdenum to rats on a low copper diet greatly enhanced by an increased intake of inorganic sulfate. They found that 1000 μg. of molybdenum daily could be given with a low sulfate diet, whereas 100 μg. proved toxic when sulfate was also given. Apparently, then, any account of the role of molybdenum in animal nutrition must take into consideration the modifying effects of other factors in the diet, and no complete account can be given until considerably more is known about the interplay of these factors.

MOLYBDENUM IN RUMINANT NUTRITION

Normal metabolism

The molybdenum content of pasture available to grazing cattle and sheep may vary from 0.01 to several hundred ppm. of the dry matter. The daily intake by the animal, consequently, may vary similarly from one place to another.

Although it has been reported that the molybdenum ingested is readily absorbed from the intestinal tract and excreted largely in the urine (70, 126), studies in sheep have shown that both the amount absorbed by the animal and the route of excretion of the absorbed molybdenum depend on the amount of inorganic sulfate in the diet (96, 100). In these experiments it was shown that the molybdenum concentration in the blood of the animal reflected the intake

[2] Personal communication.

TABLE 1

Steady values of blood molybdenum concentration attained in sheep on a daily sulfate intake of 1.8 g. at several levels of molybdenum intake

Daily Mo Intake	Blood Mo
mg.	*µg/100 ml.*
0.4	2
1.4	7
5.4	26
19.5	112
48.2	243
95.9	495

TABLE 2

Steady values of blood molybdenum concentration attained in sheep on a daily molybdenum intake of 15 mg. at several levels of sulfate intake

Daily Sulfate Intake	Blood Mo
g.	*µg/100 ml.*
1.1	114
1.8	78
3.1	28
5.7	29

TABLE 3

Urinary excretion of molybdenum and changes in blood-molybdenum concentration after administration of 11 g. potassium sulfate per os *to a sheep with daily intake of 10 mg. molybdenum and 1.3 g. sulfate*

Time After Dose of Sulfhate	Blood Mo	Mo in Urine
hr.	*µg/100 ml.*	*mg./24 hr.*
0	250	0.5
24	130	22.8
48	110	11.5
72	130	4.2

when the inorganic sulfate intake was constant, but the actual concentration for any given molybdenum intake was dependent upon the amount of sulfate in the diet. Some typical figures are given in tables 1 and 2.

If a sheep on a constant molybdenum intake is given a dose of an inorganic sulfate, either by mouth or parenterally, excretion of molybdenum in the urine will rise rapidly and the blood-molybdenum concentration will fall. The order of these effects in one experiment is shown in table 3. The rate of molybdenum loss in the urine during the first 48 hours after administration of the sulfate (table 3) greatly exceeded intake during this period and accounted for the fall in blood molybdenum. The amount of molybdenum excreted in the feces is also found to be increased by administration of sulfate, which indicates a reduction in the rate of molybdenum absorption from the gut.

TABLE 4

Total molybdenum content of tissues of sheep maintained for 35 days at several levels of molybdenum and sulfate intake

Tissue	Mo Content at Different Daily Mo and SO_4 Intakes			
	0.3 mg. Mo		20.8 mg. Mo	
	0.9 g. SO_4	6.3 g. SO_4	0.9 g. SO_4	6.3 g. SO_4
	mg.	*mg.*	*mg.*	*mg.*
Liver	1.58	0.48	5.19	1.93
Kidney	0.17	0.02	1.17	1.32
Spleen	0.52	0.02	0.57	0.14
Heart	0.18	0.01	0.94	0.04
Lung	0.65	0.09	3.96	0.42
Muscle	5.84	0.08	28.6	1.92
Brain	0.01	0.01	0.09	0.01
Skin	6.62	1.50	58.9	3.44
Wool	15.2	0.99	26.9	1.14
Small intestine	0.26	0.03	0.88	0.79
Caecum	0.24	0.01	1.64	0.58
Colon	0.63	0.04	4.21	0.62
Skeleton	61.0	13.0	164.0	16.0
Total	92.9	16.3	297.1	28.4

If the same molybdenum intake is continued but no further sulfate given, within a few days the urinary excretion of molybdenum will fall and the blood-molybdenum level rise again to the preexperiment figures.

On the other hand, if sulfate administration is continued as a daily dose, the blood-molybdenum level will continue to fall until it reaches a steady value dependent on the sulfate intake, but the amount of molybdenum excreted in the urine will constitute a lower proportion of the intake than it did before adminstration of the sulfate. These effects of inorganic sulfate in reducing molybdenum absorption and increasing the loss of stored molybdenum are reflected in a lower tissue content of molybdenum in sheep on a high sulfate intake. Table 4 compares the molybdenum content of the major tissues of animals on high and low sulfate intakes at two levels of molybdenum intake.

During the 35 days of this experiment the difference between the total molybdenum intakes of the sheep on 0.9 mg. daily and those on 6.3 mg. daily was 718 mg. This resulted in an increased storage of 204 mg. in the animals on a low sulfate intake and an increase of only 12.1 mg. in animals on the higher sulfate intake. Thus, whereas 28 per cent of the dose was retained when the sulfate intake was 0.9 g. a day, only 1.7 per cent was retained when the sulfate intake was 6.3 g. a day.

Molybdenum-copper interrelationships

The resemblance of symptoms of the disease known as "teart" in England (126) to those exhibited by cattle in certain copper-deficient areas in Holland

(127) led to the empirical and successful use of copper sulfate in the treatment of "teart." The observation that continued administration of molybdates to cattle over long periods resulted in a depletion of their copper reserves led to the experimental observation that small quantities of molybdates given to sheep exerted a distinct limitation on their copper retention (72). It was then suggested that conditions which resulted in very low molybdenum content of pastures might result in an excessive accumulation of copper by sheep followed by chronic copper poisoning and subsequent death; and conversely, in areas where diseases curable by copper administration were observed on pastures of apparently normal copper content, a copper availability to the animal might possibly be limited by a high pasture-molybdenum.

Subsequent investigations in New Zealand indicated that the disease of cattle known as "peat scours" occurred in areas where the molybdenum content of pastures was moderately high. Although molybdenum content was not so high as in pastures on which "teart" occurred in Somerset, the lower copper content of the pastures and the consequent depletion of the animal's copper reserves were sufficient, in view of the known effect of molybdenum in limiting copper storage, to account for the scouring at the lower molybdenum intake. Other conditions in stock in New Zealand associated with interference in copper metabolism by an abnormal molybdenum intake are unthriftiness and loss of coat color in beef cattle and ataxia in lambs, conditions recently reviewed by Cunningham (293).

Continuation of our own laboratory studies of the effects of molybdenum on copper metabolism in sheep has resulted in the following conclusion: Although for any particular diet there is a quantitative relationship between the molybdenum content of the diet and the amount of copper stored by the animal, and for a given copper intake the sheep could be on either positive or negative copper balance, depending on the molybdenum intake, the magnitude of the effect of molybdenum is, in turn, dependent on the amount of inorganic sulfate in the diet (95). These studies indicated that neither molybdenum nor sulfate alone interfered with copper retention, and that the effectiveness of either increased to a maximum as the intake of the other was increased (99). It was possible for the copper reserves of the sheep to increase on comparatively low copper intakes when the molybdenum and sulfate content of the diet was low, and, conversely, for the animal's copper reserves to be depleted, even to the level of a clinical copper deficiency (391), when copper intake was normal to high and molybdenum and sulfate intakes were also high. It has been shown also that if the molybdenum intake of sheep is increased to the high levels that occur in the pastures responsible for the scouring diseases of cattle in England and the United States, the lesion in the fleece, characteristic of copper deficiency, will appear immediately, provided sulfate intake is also high (98). Even this "physiological copper deficiency," however, does not appear unless both molybdenum and sulfate intakes are high. Under these conditions fleece lesion is the only sign of copper deficiency; liver copper does not become depleted, and blood copper does not fall. Blood copper, in fact, is elevated above normal, which is interpreted to be

TABLE 5

Change in liver-copper concentration during a 98-day period in sheep on a basal ration of 90/10 chaffed oaten/lucerne hay mixture when supplements indicated were added

Supplements Added	Change in Liver-Copper Concentration at Different Daily Mo Intakes	
	7.5 mg. Mo	25 mg. Mo.
	ppm.	*ppm.*
Mo only	+308	+193
Mo + SO_4	+65	+2
Mo + SO_4 + Mn	+215	+18
Mo + Mn	+268	+115

Daily intakes supplied by basal ration: SO_4^{--}, 1.7 g.; Mo, 0.3 mg.; Mn, 135 mg.
Supplements added daily: SO_4^{--}, 3.8 g.; Mo, 7.5 or 25 mg.; Mn, 165 mg.
Total daily copper intake 10 mg.

TABLE 6

Change in liver-copper concentration during a 98-day period in sheep on a basal ration of 90/10 chaffed oaten/lucerne hay mixture when supplements indicated were added

Supplements Added	Change in Liver-Copper Concentration at Different Daily Mo Intakes	
	7.5 mg. Mo	25 mg. Mo
	ppm.	*ppm.*
Mo only	+308	+193
Mo + SO_4	+65	+2
Mo + gluten	+83	+23
Mo + gluten + Mn	+5	−53

Daily intakes supplied by basal ration: SO_4^{--}, 1.7 g.; Mo, 0.3 mg.; Mn, 135 mg.; and protein, 120 g.
Supplements added daily: SO_4^{--}, 3.8 g.; Mo, 7.5 or 25 mg.; Mn, 165 mg.; and gluten, 100 g.
Total daily copper intake 10 mg.

an indication that the very high molybdenum and sulfate intake interferes with copper excretion.

More recent studies[3] indicate that still other dietary factors may play a part in the interrelationship between molybdenum and copper in ruminant nutrition. For example, it has now been found that even in presence of adequate sulfate, molybdenum will not interfere with copper retention in sheep if their diet also contains a high manganese content (table 5). On present evidence this appears not to be a direct effect of manganese in increasing copper retention and so balancing out the limiting effect of molybdenum and sulfate, but rather a direct blocking of this limiting effect. If the diet of the sheep is sufficiently high in protein, sufficient of the sulfur of the protein apparently will be oxidized to sulfate to act effectively with molybdenum in limiting copper retention. This effect is shown in table 6. If, however, in addition to molybdenum and excess protein, the diet also contains a high manganese content, table 6 indicates another

[3] Author's unpublished data.

effect on limitation of copper retention attributable to molybdenum and manganese and some product of protein metabolism other than sulfate. These effects are being investigated further, but they serve to illustrate the need for more intensive study of the dietary factors that may be involved in the effects of molybdenum on the copper metabolism of the ruminant.

MOLYBDENUM IN NONRUMINANTS

Comparatively few studies have been made on the molybdenum metabolism of monogastric animals. Observations reported in the literature are sporadic and disconnected, the effects on molybdenum metabolism of dietary sulfate apparently have not yet received any attention.

The examination of the molybdenum requirements of the rat by Teresi *et al.* (335) has already been referred to. A later study by Nielands *et al.* (264) included some observations on the tissue distribution during short periods after oral administration of Mo 99. They found slightly higher amounts of molybdenum in kidney and bone after 2 days and made the interesting observation that catechol given simultaneously with the molybdenum considerably increased the molybdenum content of all tissues.

Shirley *et al.* (309) in a study with radio-molybdenum found that very little of an oral dose of molybdenum administered to pregnant sows was transferred to the fetuses; most of the molybdenum dose was excreted in the urine.

Most of the observations on molybdenum in monogastric animals have been concerned with the toxic effects of very high intake levels and the protection offered by copper. Jeter and Davis (200) did observe retarded growth in rats when the diet contained 20–140 ppm. of molybdenum and only 5 ppm. of copper, but a dietary copper concentration of 20 ppm. protected against 80 ppm. of molybdenum. In rabbits, Arrington and Davis (31) observed no ill effects of molybdenum concentrations up to 500 ppm. in the diet when the copper concentration was 16.4 ppm., but 1000 ppm. of molybdenum produced gross toxic effects characterized by loss of weight, alopecia, dermatosis, anemia, and death in 50–55 days. They observed that in some young rabbits a deformity of the front legs developed. The protection afforded by copper against molybdenum toxicity in nonruminants has been established by a number of workers, but in studies with radiomolybdenum and radiocopper in rats and swine, Kulwich *et al.* (217) found that addition of molybdenum to the diet increased materially the copper content of tissues; they were unable to observe any protection against the toxic effects of 1000 ppm. Mo in the diet of young rats when the copper concentration was raised to 20 ppm.

Inconsistencies in these observations of the quantitative interrelationships between molybdenum and copper in monogastric animals when the sulfate intake is not taken into consideration suggest strongly that the effects of at least this dietary constituent should be examined in these species. The only pointer in the literature to suggest any parallel with the observations on the effect of sulfate in ruminants is the passing observation of de Renzo *et al.* (88), that sodium tungstate added to the diet of young rats is apparently able to inhibit the stimulatory effect of molybdenum on the intestinal xanthine oxidase activity.

Whether or not the role of sulfate in copper-molybdenum interactions in ruminants is paralleled in other species of animals, dietary factors other than molybdenum obviously will be found to have a profound modifying effect on the relationship between these two elements. In view of the more recent observations in this laboratory, three significant observations in the literature seemingly might well justify further investigation.

The first is the reported observation of Gray and Daniel (153) that methionine proved to be more effective than copper in protecting rats on a milk powder ration from the toxic effects of molybdenum.

The second is the Nielands *et al.* (264) paper already referred to. In addition to the protective effects of copper against molybdenum intoxication, these workers observed that although iron, zinc, and cobalt exerted no detectable protective effect, dried whole liver at a level of 5 per cent in the diet gave a very high degree of protection, although its copper content was insufficient to account for this effect.

The third observation concerns manganese and the striking resemblance between signs of manganese deficiency in rabbits and the deformity of the foreleg referred to by Arrington and Davis (31) as one of the signs of molybdenum intoxication in young rabbits.

It may well be that further inquiry will reveal a connection not only between these observations in the monogastric animal but also with our own recent findings in sheep. That is, not only is the effect of molybdenum and sulfate in limiting copper retention in the sheep antagonized by a high manganese intake, but addition of molybdenum and manganese exerts a severely limiting effect on copper retention when sheep are on a high protein diet.

MOLYBDENUM CONTENT OF ALFALFA IN RELATION TO DEFICIENCY SYMPTOMS AND RESPONSE TO MOLYBDENUM FERTILIZATION

H. M. REISENAUER

Washington Agricultural Experiment Station[1]

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Low levels of available soil molybdenum limit the growth of alfalfa and other legume crops on the Couse soils of northeastern Washington. Although beneficial effects from application of molybdenum to alfalfa have been reported by other workers,[2] considerable disagreement exists as to the exact nature of plant symptoms and the concentration of molybdenum in the plant necessary for normal growth and development. Accordingly, investigations were conducted to evaluate plant deficiency symptoms and tissue analysis as diagnostic techniques.

MATERIALS AND METHODS

The experiments reported were conducted in 1953 and 1954 on Couse silt-loam in northeastern Washington. The Couse soil, developed under forest vegetation, has a pH of 5.7 to 6.0 in the surface. Its average cation-exchange capacity per 100 g. at pH 7.0 is 13.6 me.; exchangeable calcium, 7.5 me.; exchangeable magnesium, 1.2 me.; and exchangeable potassium, 0.4 me. Most of the area has suffered moderate to severe erosion. Cereal crops growing in this soil respond to nitrogen and sulfur fertilizers.

Although plants of some recently established stands of alfalfa in the area failed to grow normally because of poor nodulation, the yield data presented here were obtained from well-nodulated plants. Normal growth and appearance of poorly nodulated plants was restored by applications per acre of 100 pounds or more of nitrogen from ammonium nitrate. Application of molybdenum fertilizer benefited growth of well-nodulated plants but had no noticeable effect on growth or appearance of plants on whose roots no nodules could be found. The degree of nodulation was not related to the level of molybdenum in the plant, which is in agreement with the work of Anderson and Thomas (11) and Walker *et al.* (356).

Fertilizer treatments of existing stands of alfalfa (*Medicago sativa*) were applied in the fall. All experimental areas received a uniform application of 100 pounds of gypsum per acre. Since uniformly deficient areas are rarely encountered, and since the deficiency pattern of an area is not related to any readily determined soil characteristic, most of the trials consisted of long, adjacent, treated and untreated strips, each 12 feet wide.

Yield data and samples of plant tops were obtained when the crop was at

[1] Scientific Paper 1451. These investigations were supported in part by a grant in aid from the Climax Molybdenum Company.

[2] References 8, 119, 140, 173, 392.

approximately 10 per cent bloom. Alfalfa hay yield was determined from the air-dry weight of plant material obtained with the aid of a power mower from 60 square feet of each plot. The plant samples were collected in paper bags and dried at 50°C., after which the plants were divided into leaves plus petioles (hereafter referred to as leaves) and stems. The dried samples were ground to pass a 1-mm. mesh screen and stored in paper containers.

Chemical analyses of plant samples included determinations of molybdenum, nitrogen, phosphorus, and manganese. Molybdenum was determined by the method of Marmoy (234) with isoamyl alcohol as the color extractant. Phosphorus was determined in a sulfuric acid–selenium digest of 0.5 g. of plant material by the colorimetric molybdivanadophosphoric acid procedure of Kitson and Mellon (209). The nitrogen analyses of the 1953 samples were made on the phosphorus digest by the Nesslerization procedure of Johnson (204). The nitrogen content of the 1954 samples was determined by the Kjeldahl procedure. Manganese determinations were made by the method of Piper (274).

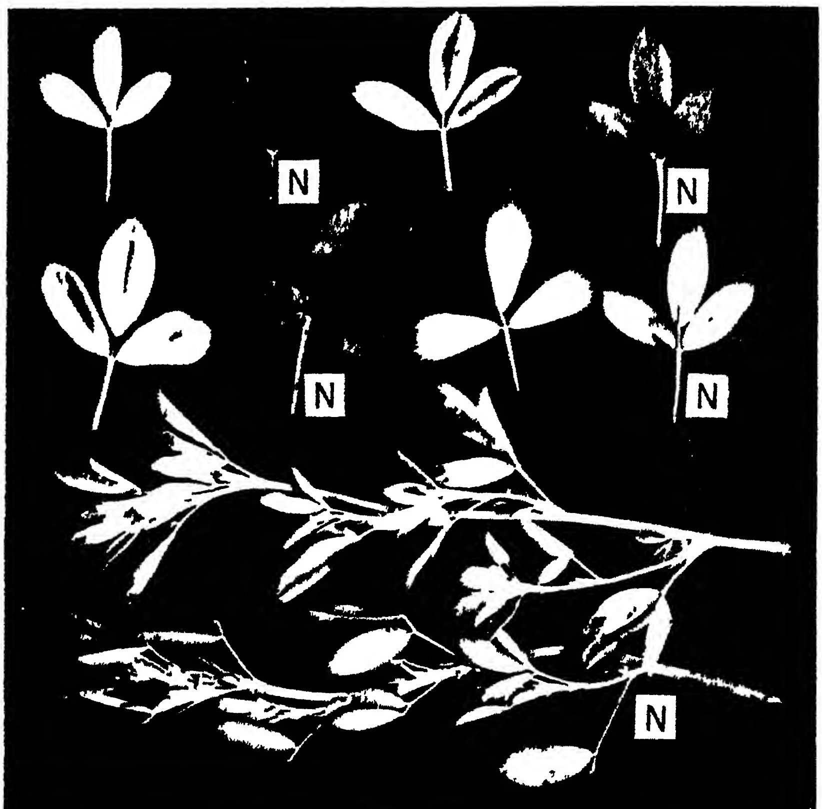

FIG. 1. MOLYBDENUM-DEFICIENT AND NORMAL ALFALFA
Normal plants identified by "N." Note pale color and chlorotic spots on the leaves of deficient plants. (Photographed with red filter.)

RESULTS AND DISCUSSION

Visual symptoms

Fields of molybdenum-deficient crops were characterized by a patchy appearance, which was the result of areas of both healthy and deficient plants. The deficient plants were stunted in growth and of pale green color. The leaves of molybdenum-deficient alfalfa plants showed pronounced chlorotic spots (fig. 1) in the interveinal tissue; these spread to include the entire leaf, which then died and dropped off. Chlorosis was most severe on the lower leaves, and markedly deficient plants retained only their upper leaves. These symptoms on field-grown alfalfa were very similar to those reported by Evans *et al.* (117) and Hewitt (173) on plants grown in culture solutions in which the nitrogen was supplied as nitrate. Marginal necrosis of the upper leaves of molybdenum-deficient alfalfa plants, reported by Evans *et al.* (117), was not observed on the Couse soil.

The symptoms which developed on field-grown alfalfa were those of nitrogen starvation. Symptom severity was related to the nitrogen content and not necessarily to the molybdenum content of the tissue (table 1). The data (table 1) were obtained from plants selected in fields with both poorly nodulated and molybdenum-responsive plants. Since nitrogen starvation of legumes may result from any one of several unfavorable conditions, visual symptoms are not a positive identification of molybdenum deficiency.

Selection of plant part for analysis

Plant analysis has been used successfully in determining the nutritional status of crops with respect to several elements (340). The technique selected for collecting plant samples for analysis depends on the purpose of the sampling and on the amount of material required for assay. Samples obtained at harvest of the crop are, in general, of the greatest utility, since they may be used in evaluating effects of the treatments on crop quality characteristics; it is also desirable to sample the plant at a readily recognizable stage of maturity. Plant samples for this study, therefore, were obtained at harvest (approximately 10 per cent bloom).

The plant part selected for analysis depended on the amount of material required for assay, the concentration range of the element in different plant parts, and the relation of the concentration of the element in the plant part to the nu-

TABLE 1

Nitrogen and molybdenum content of alfalfa plants showing nitrogen-starvation symptoms to varying degrees

Symptoms	Leaf N	Leaf Mo
	per cent	*ppm.*
None	3.61	0.34
Mild	2.98	0.26
Moderate	2.68	0.26
Severe	2.63	0.28

tritional status of the plant. Stout and Meagher (329) found that molybdenum is accumulated in the interveinal areas of the plant. The relationship between the molybdenum content of alfalfa stems and leaves in the present work is presented in figure 2. The concentration of molybdenum in the leaves is approximately four times that of the stems. This, combined with the wide variation in the leaf-to-stem ratios of alfalfa, might account in part for the failure of other workers (11, 119) to obtain significant relations between molybdenum analysis and response to molybdenum fertilization. The ratio of alfalfa leaves to stems was found to vary from 0.7 to 1.8. Low leaf-to-stem ratios were associated with high-yielding alfalfa and with plants exhibiting severe deficiency symptoms. It would be quite possible to obtain identical molybdenum concentrations in whole plant samples taken from a nondeficient, vigorous, dense stand of alfalfa and a less dense stand of deficient plants. In addition, the leaves exhibited a much greater range in molybdenum content than did the stems. It was considered desirable, therefore, to relate molybdenum response to leaf rather than to whole plant analyses. No further subdivision of plant parts was attempted since the size of the sample required (approximately 10 g. of plant material is required for analysis in the range of 0 to 0.5 ppm. molybdenum) would limit the value of any relationships.

Alfalfa yield related to leaf molybdenum

Yield data were obtained from one replicated and eight strip-type experiments. The replicated experiment was designed to determine the effect of rate of application of molybdenum on yield and chemical properties of alfalfa hay. The molybdenum treatments were applied to plots 8 by 25 feet and replicated twice. The data from this experiment are presented in table 2. Yield increases from molybdenum fertilization were just short of statistical significance at the 5 per cent probability level (F calculated = 7.59, F required = 7.71). Near-maximum yields were obtained from molybdenum applications of 0.8 pound per acre. The average yields from the strip trials conducted in the area were 0.81 ton per acre from the untreated areas and 1.12 tons per acre from areas receiving 0.8 pound of molybdenum per acre.

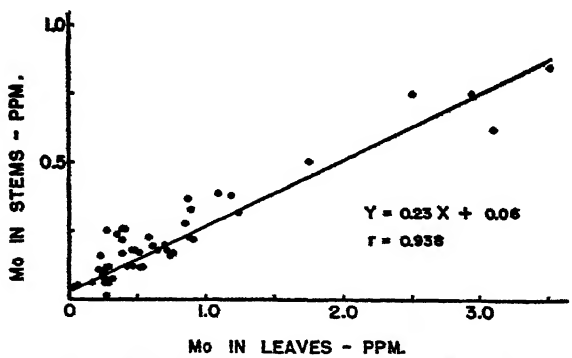

Fig. 2. Relation Between Concentration of Molybdenum in Stems and Leaves of Alfalfa

TABLE 2

Effect of rate of application of molybdenum on yield of alfalfa hay, and on molybdenum, nitrogen, phosphorus, and manganese content of alfalfa leaves

Mo Applied	Hay Yield	Leaf Analyses			
		Mo	N	P	Mn
lb./A.	*ton/A.*	*ppm.*	*per cent*	*per cent*	*ppm.*
0	1.06	0.27	2.77	0.25	62
0.8	1.27	0.68	3.03	0.26	61
1.6	1.39	2.01	3.16	0.25	57
3.2	1.43	3.51	3.10	0.26	57
6.4	1.39	11.84	3.10	0.26	61
L.S.D. (0.05)	N.S.	—	0.10	N.S.	N.S.
L.S.D. (0.01)	N.S.	—	0.17	N.S.	N.S.
Coefficient of variation........%	10.5	—	1.2	7.9	6.8

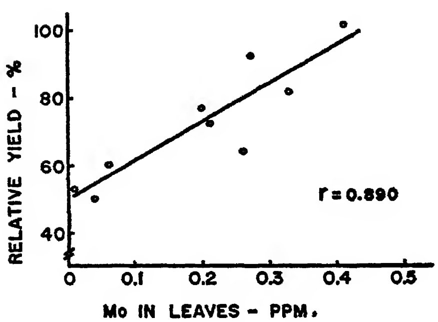

FIG. 3.

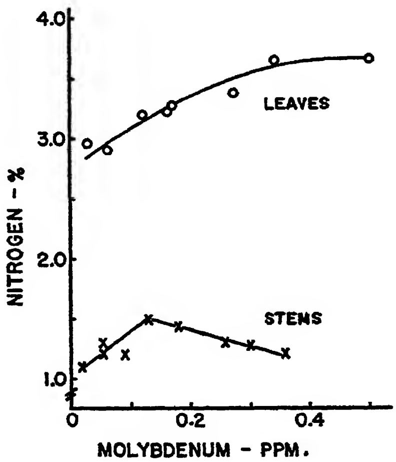

FIG. 4.

FIG. 3. RESPONSE OF ALFALFA TO MOLYBDENUM FERTILIZATION RELATED TO MOLYBDENUM CONTENT OF LEAVES FROM UNTREATED AREA

Relative yield = yield from untreated area/yield from molybdenum-fertilized area.

FIG. 4. RELATIONS BETWEEN NITROGEN AND MOLYBDENUM IN ALFALFA LEAVES AND STEMS

The relation between relative hay yield (yield from untreated area/yield from molybdenum-treated area) and the molybdenum content of alfalfa leaves from the untreated area is shown in figure 3. Yield increases from molybdenum fertilization would not be expected at leaf-molybdenum levels greater than 0.4 to 0.5 ppm. The data plotted include only one location at which no yield increase was obtained. Leaf molybdenum levels from the adjacent treated areas (0.8 pound Mo/acre) were between 0.4 and 0.6 ppm. at four of the locations and between 0.6 and 0.9 ppm. at the other five locations. The relatively high hay yields obtained at very low leaf-molybdenum levels (less than 0.1 ppm.) indi-

cates that the alfalfa plant, acting as a nonlegume, has a much lower requirement for this nutrient than do the nodule bacteria.

The data of Evans and Purvis (119) do not support the establishment of 0.5 ppm. leaf molybdenum as an adequate level for alfalfa. They reported yield increases of 13 per cent and 8 per cent from molybdenum fertilization with alfalfa-top-molybdenum levels of 0.77 and 0.85 ppm., respectively. The alfalfa-leaf-molybdenum levels in their trials would be considerably higher. Other workers (284, 330) have reported 0.5 ppm. of molybdenum in plant tissue as an adequate level. This apparent anomaly may result from a manganese-molybdenum antagonism, as suggested by Walker *et al.* (356). The leaf-manganese levels reported in table 2 are well below the toxic level (251). Molybdenum fertilization had no effect on the manganese or phosphorus content of alfalfa leaves.

Nitrogen-molybdenum relations

Molybdenum fertilization increased the nitrogen content of nodulated alfalfa growing on the Couse soil. The magnitude of this increase and its relation to the molybdenum content of the plant tissue are illustrated in figure 4. The data plotted are those obtained in 1953. Maximum nitrogen levels in alfalfa leaves were obtained at 0.4 ppm. molybdenum. A similar relation between the nitrogen and molybdenum content of alfalfa leaves was obtained in 1954 and has been reported in white clover (356). The highest nitrogen content in alfalfa stems was obtained at 0.15 ppm. molybdenum. The relation obtained with the stems is a function of their size. Molybdenum fertilization increased the total yield of alfalfa and stem diameter and length. The larger stems, which are more fibrous, contain proportionately less protein.

The occurrence of both yield and nitrogen maxima with leaf-molybdenum levels near 0.5 ppm. supports the establishment of 0.5 ppm. leaf molybdenum as an adequate level in alfalfa.

SUMMARY

Experiments were conducted on a molybdenum-responsive soil of northeastern Washington to relate the molybdenum content of alfalfa to severity of deficiency symptoms and to response to fertilization with this nutrient.

The visual symptoms developed on field-grown alfalfa were an expression of nitrogen starvation and not a positive identification of molybdenum deficiency. Unnodulated alfalfa plants did not benefit from molybdenum fertilization.

Where nodulation was satisfactory, increases in yield and nitrogen content of alfalfa hay were obtained from molybdenum fertilization. Maximum yields and protein content of alfalfa plant tops were associated with leaf-molybdenum levels of 0.5 ppm. or more.

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INFLUENCE OF SOME COMMON SOIL FUNGI ON GROWTH OF CITRUS SEEDLINGS

J. P. MARTIN, L. J. KLOTZ, T. A. DEWOLFE, AND J. O. ERVIN

University of California Citrus Experiment Station[1]

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Growth of citrus plants in most California soils causes reduced growth of subsequent plantings of the same species (12). The degree of growth reduction has been observed to vary tremendously. Unpublished greenhouse tests indicated that growth of citrus seedlings ranges from slightly better to more than 100 per cent better in noncitrus soils (soils never before planted to citrus) than in adjacent old citrus soils.

Reduction of growth was greater in a soil containing excess lime than in an acid soil (13), and a deficiency or excess of K or an excess of Na intensified the growth reduction (3). Parasitic nematodes and fungi also limit growth (1, 4, 5, 6, 10). Variation in growth may result from differences in the balance between plant parasites and other microorganisms including inhibitors of the parasites. The relative growth and activity of parasites are reduced by associated organisms that compete for food and space or destroy the parasites directly, and possibly by antibiotics produced by some of them, although this possibility has not been definitely established (8, 14).

Various crop rotations, green manure crops, or additions of organic matter to the soil will sometimes aid in the control of root parasites (7, 9). It is believed that part of the effect of the organic material is the stimulation of a soil population antagonistic to the detrimental forms.

The antagonistic relations among the soil organisms may be subtle, as indicated by Bliss (2) and Darley and Wilbur (3). These investigators found that soil fumigation with carbon disulfide usually gave good control of Armillaria root rot, although the parasite was not killed by the treatment. After fumigation, *Trichoderma viride* parasitized and destroyed *Armillaria mellea*. The fumigation treatment apparently increased the activity of *T. viride* or possibly it destroyed some antagonist of this fungus.

If detrimental soil organisms reduce the rate of growth of second plantings of citrus, then presumably they are operative in old citrus orchards still in existence. In this case different microbial species or populations may possible influence growth of the plant through antagonistic or competitive actions with detrimental species. To check this possibility, studies were initiated to determine whether different species of common soil fungi, either singly or in various combinations,

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do influence growth of citrus plants. Although most of the fungi used were soil saprophytes, a few species, found in old citrus soils and capable of parasitizing some plants, were used to determine their effect on citrus seedlings under the conditions of the study.

MATERIALS AND METHODS

All tests were carried out in 3-gallon pots in the greenhouse, and all treatments were replicated three or four times. Soil at a moisture content suitable for screening but not dry was sieved, mixed, and placed in 5-gallon milk cans. To the soil in each container was added 25 ml. of propylene oxide, and the lids were immediately placed in position and secured. After 5 days the fumigated soil was spread in a thin layer on wrapping paper and allowed to stand for 7 days; it was then placed in the pots. As the pots were being filled spore suspensions of the desired fungi were added to the soil at four levels. After the treated soil was moistened and incubated for 1 week, two sweet orange seedlings with bare roots were planted in each pot. The plants were grown 6 to 9 months.

The soil fungi were isolated and counted by the dilution plate technique, using peptone dextrose–rose bengal–streptomycin medium adjusted to pH 7 (11). Two months after inoculation, the soil was sampled by removing the top inch and taking a slice from the 1- to 5-inch depth. At harvest time the soil for plating was shaken from the feeder roots after removal of the plants from the pots and removal of any clumps or masses of adhering soil.

RESULTS

Test 1

The effect of soil fumigation and of inoculation with fungus species on growth of sweet orange seedlings in old citrus and noncitrus Yolo sandy loam is reported

TABLE 1

Effect of fumigation and inoculation with species of soil fungi, separately and in various combinations, on growth of sweet orange seedlings in Yolo sandy loam (test 1)

Soil Treatment	Dry Weight of Tops*	
	Old citrus soil	Noncitrus soil
	g.	g.
1. NONE (check)	25	39
2. FUMIGATED	39	38
FUMIGATED AND INOCULATED WITH:		
3. *Pyrenochaeta* sp.	42	44
4. *Fusarium oxysporum*	35	33
5. *Fusarium solani*	40	43
6. *Penicillium funiculosum*	40	46
7. *F. oxysporum*, *F. solani*, and *Pyrenochaeta* sp.	43	43
8. *F. oxysporum*, *F. solani*, *Pyrenochaeta*, sp. and *P. funiculosum*	40	39

* Average per 3-gallon pot of soil. L.S.D. 5% = 7 g.

TABLE 2

Effect of fumigation and inoculation with various species of fungi on number and kind of fungi in Yolo sandy loam 2 and 8 months after inoculation (test 1)

Fungus	Soil Treatment*															
	Old citrus soil								Noncitrus soil							
	1	2	3	4	5	6	7	8	1	2	3	4	5	6	7	8
	Approx. number of fungi in thousands/g. soil 2 months after inoculation															
	149	2	31	6	5	470	19	85	70	5	20	33	29	190	28	180
	Approximate percentage concentration of fungi on plates															
Fusarium spp.	7	–	–	–	–	–	–	–	38	8	–	–	–	–	–	–
F. oxysporum	2	–	–	60	–	–	23	4	–	–	–	99	–	–	1	1
F. solani	21	8	1	–	100	–	30	48	–	–	–	–	100	–	80	9
Penicillium funiculosum	1	2	–	–	–	100	–	45	–	–	–	–	–	100	–	85
P. nigricans	8	55	52	–	–	–	–	–	30	–	–	–	–	–	7	2
Pyrenochaeta sp.	5	–	12	30	–	–	47	0	–	–	100	–	–	–	1	2
Stysanus stemonites	13	–	–	–	–	–	–	–	–	72	–	–	–	–	–	–
	Appprox. number of fungi in thousands/g. of soil 8 months after inoculation															
	200	134	38	18	16	690	17	141	126	47	43	12	49	320	29	194
	Approx. percentage concentration of fungi on plates															
Fusarium spp.	11	1	–	–	–	–	–	–	19	–	–	1	–	–	–	–
F. oxysporum	6	–	–	6	–	–	2	1	–	–	–	27	–	–	2	–
F. solani	6	6	22	30	75	1	68	12	7	34	22	34	71	1	67	9
Penicillium funiculosum	–	46	33	–	–	99	5	83	–	–	–	1	–	94	3	89
Pullaria pullulans	–	–	–	42	11	–	7	2	3	33	56	27	24	–	10	–
Pyrenochaeta sp.	–	–	2	–	4	–	15	1	–	–	21	–	–	–	24	1
Thielaviopsis basicola	–	38	–	17	3	–	3	1	7	4	–	4	3	1	1	–

* See table 1.

in table 1. Destruction of the existing population in the old citrus soil so increased plant growth that it became comparable to plant growth in the noncitrus soil. Inoculation of fumigated soil with a strain of *Fusarium oxysporum* appeared to reduce growth slightly in both soils. Inoculation with *Pyrenochaeta* sp., *Fusarium solani*, or *Penicillium funiculosum*, alone or with all cultures in various combinations, did not significantly influence seedling growth.

At 2 months, the fungus populations (table 2) of the inoculated soils consisted largely of the introduced species. In a few pots, however, *Penicillium nigricans* or *F. solani* also had become established. After 8 months, additional species including *F. solani*, *P. funiculosum*, *Pullularia pullulans*, and *Thielaviopsis basicola* had become established in one or more of the soils that had not been inoculated with them. *P. funiculosum* almost completely resisted the establishment of other species; *Pyrenochaeta* sp. disappeared from one soil.

TABLE 3

*Effect of fumigation and inoculation with species of soil fungi, separately and in various combinations, on growth of sweet orange seedlings in Yolo sandy loam (test 2)**

Soil treatment	Dry weight of tops†
	g.
1. CHECK (none)	17
2. FUMIGATED	24
FUMIGATED AND INOCULATED WITH:	
3. *Pyrenochaeta* sp.	25
4. *Thielaviopsis basicola*	5
5. *Fusarium solani*	24
6. *Pythium ultimum*	21
7. *Pyrenochaeta* sp., *T. basicola*, *F. solani*, and *P. ultimum*	13

* Only old citrus soil used.
† Average per 3-gallon pot of soil. L.S.D. 5% = 4g.

Test 2

Tables 3 and 4 show the influence of several fungus species which have been found to increase in concentration in some soils cropped to citrus in the greenhouse, on growth of sweet orange seedlings in Yolo sandy loam, and the nature of the fungus population following inoculation. After 2 months the only fungus colonies appearing on the dilution plates from the soil inoculated with *Pyrenochaeta* sp., *Thielaviopsis basicola*, or *Fusarium solani* consisted of the particular species used for inoculation. No fungi capable of growing on the peptone dextrose–rose bengal–streptomycin medium were found in the noninoculated fumigated soil. *F. solani* became established in the soil inoculated with *Pythium ultimum*, and isolation technique, with fresh apples as the discriminating medium, showed that *P. ultimum* was present in this soil. *Pyrenochaeta* sp. did not survive in soil inoculated with all four species. After 8 months the fungus populations were still essentially the same as they were at 2 months.

The establishment of *F. solani* or *Pyrenochaeta* sp. did not influence growth of the seedlings. *Pythium ultimum* may have slightly reduced growth. The plants in this treatment, especially during early stages of growth, were small and pale; later, they improved in color and vigor. *Thielaviopsis basicola* markedly reduced seedling growth, but when this organism was combined with *F. solani* and *P. ultimum*, the degree of growth retardation was appreciably reduced.

Test 3

The results of a third test with Yolo sandy loam and 15 different common soil fungi are reported in table 5. All the fungi except one, *Epicoccum purpurascens*, were present 2 months after inoculation. Eleven species constituted the only forms isolated from the particular soil inoculated with each. After 8 months the populations were largely the same, but a few additional types, primarily *Fusarium solani* and *Penicillium nigricans*, had developed in a few soils. None of the cultures tested significantly influenced growth of the seedlings.

TABLE 4

Effect of fumigation and inoculation with various species of fungi on number and kind of fungi in old citrus Yolo sandy loam 2 and 8 months after inoculation (*test 2*)

Fungus	Soil treatment*						
	1	2	3	4	5	6†	7†
	Approx. number of fungi in thousands/g. of soil 2 months after inoculation						
	145				130		380
	Approximate percentage concentration of fungi on plates						
Aspergillus niger	6	0	0	0	0	0	0
A. versicolor	3	0	0	0	0	0	0
Fusarium spp.	28	0	0	0	0	0	0
F. solani	16	0	0	0	100	100	90
Pullularia pullulans	27	0	0	0	0	0	0
Pyrenochaeta sp.	8	0	100	0	0	0	0
Thielaviopsis basicola	0	0	0	100	0	0	10
Stachybotrys atra	7	0	0	0	0	0	0
Stysanus stemonites	2	0	0	0	0	0	0
	Approx. number of fungi in thousands/g. of soil 8 months after inoculation						
	168	3	6	14	40	4	122
	Approx. percentage concentration of fungi on plates						
Aspergillus niger	0	25	0	0	0	0	0
Fusarium oxysporum	0	50	0	0	0	0	0
F. solani	32	25	0	0	100	80	92
Gliocladium penicilloides	0	0	0	8	0	0	0
Pullularia pullulans	16	0	0	0	0	0	0
Pyrenochaeta sp.	8	0	90	0	0	0	0
Thielaviopsis basicola	0	0	0	92	0	0	8
Stachybotrys atra	6	0	0	0	0	0	0
Stysanus stemonites	3	0	0	0	0	0	0

* See table 3.
† Lemon test for *Pythium* positive.

Test 4

Holtville silty clay loam was used in a fourth test (see table 6 and fig. 1). Because of the striking growth reduction caused by *Thielaviopsis basicola*, this organism was used for soil inoculations in combination with a variety of soil fungi. In addition, two citrus parasites, *Phytophthora citrophthora* and *P. parasitica*, were used. Chemical analyses were made on leaf samples collected from the seedlings at harvest time. Two months after treatment, virtually no fungi except those with which the soils had been inoculated were recovered from the fumigated soils. This condition persisted, and in only relatively few soils were fungi other than the introduced ones recovered after 8 months. *Stemphylium piriforme*, however, did not become established in the inoculated fumigated soil.

TABLE 5

*Effect of fumigation and inoculation with species of soil fungi, on growth of sweet orange seedlings in Yolo sandy loam (test 3)**

Soil treatment	Dry weight of tops†
1. CHECK (none)	23
2. FUMIGATED (none)	38
FUMIGATED AND INOCULATED WITH:	
3. *Volutella* sp.	40
4. *Cunninghamella echinulata*	44
5. *Monotospora brevis*	38
6. *Myrothecium verrucaria*	38
7. *Cylindrocarpon radicicola*	40
8. *Penicillium frequentans*	40
9. *Aspergillus fumigatus*	38
10. *Fusarium* sp.	38
11. *Penicillium lapidosum*	40
12. *Gliocladium penicilloides*	41
13. *Aspergillus nidulans*	39
14. *Epicoccum purpurascens*	41
15. *Acrostalagmus cinnabarinus*	44
16. *Trichoderma viride*	42
17. *Fusarium solani*	41

* Only old citrus soil used.
Average dry weight per 3-gallon pot of soil. L.S.D. 5% = 5 g.

TABLE 6

Effect of fumigation and inoculation with species of soil fungi, separately and in various combinations, on growth and on chemical constituents of leaves of sweet orange seedlings in Holtville silty clay loam from an old tangerine grove (test 4)

Soil treatment	Dry weight of tops*	Leaf constituents†				
		Ca	K	Na	Mn	Fe
	g.	%	%	%	ppm.	ppm.
1. NONE (check)	6	5.3	2.4	0.06	9	53
2. FUMIGATED	26	2.8	1.6	0.04	19	51
FUMIGATED AND INOCULATED WITH:						
3. *Fusarium oxysporum*	25	2.4	1.6	0.02	28	54
4. *Stemphylium piriforme*	25	2.4	1.6	0.02	22	80
5. *Sclerotium* sp.	22	2.4	1.7	0.02	18	39
6. *Pythium ultimum*	20	2.6	1.6	0.02	23	81
7. *Fusarium solani* and *Pyrenochaeta* sp.	21	2.6	1.8	0.02	19	45
8. *Phytophthora citrophthora* and *P. parasitica*	22	2.7	1.6	0.02	22	66
9. *Thielaviopsis basicola*	6	2.8	2.0	0.06	24	48
10. *T. basicola* and *Fusarium solani*	8	3.1	2.0	0.08	19	44
11. *T. basicola and Penicillium funiculosum*	7	3.4	1.9	0.09	26	48
12. *T. basicola* and *Trichoderma viride*	9	2.8	1.9	0.04	28	45
13. *T. basicola* and *Stachybotrys atra*	12	3.0	1.8	0.03	30	45
14. *T. basicola* and *Penicillium nigricans*	14	2.6	1.7	0.03	28	48
15. *T. basicola* and *Penicillium chrysogenum*	7	3.1	2.4	0.09	22	40

* Average per 3-gallon pot of soil. L.S.D. 5% = 4 g.
† No significant differences in percentages of leaf P, Mg, Cu, and Zn.

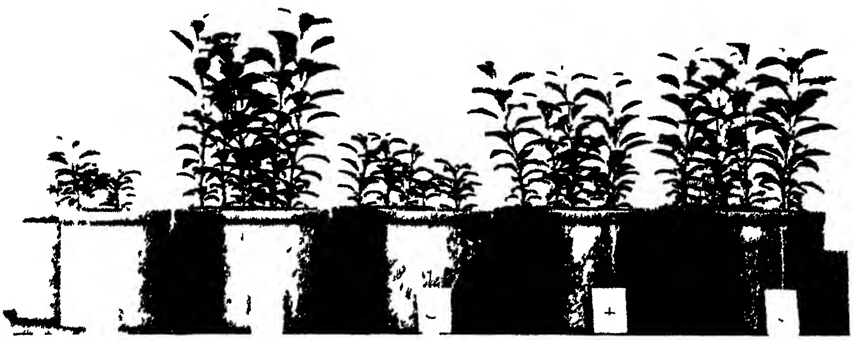

FIG 1 EFFECT OF SOIL FUMIGATION AND INOCULATION WITH SOIL FUNGI ON GROWTH OF SWEET ORANGE SEEDLINGS IN OLD CITRUS HOLTVILLE SILTY CLAY LOAM

Pot 1, original old citrus soil; pot 2, soil fumigated; pot 3, soil fumigated and inoculated with *Thielaviopsis basicola*; pot 4, soil fumigated and inoculated with *T. basicola* and *Penicillium nigricans*; pot 5, soil fumigated and inoculated with *Phytophthora citrophthora* and *P. parasitica*.

Again, in this soil, *Pythium ultimum* slightly reduced seedling growth, the *T. basicola* greatly retarded growth. In combination with *Fusarium solani*, *Penicillium funiculosum*, *Trichoderma viride*, or *Penicillium chrysogenum*, *T. basicola* decreased growth almost to the same degree as when used alone. In combination with *Stachybotrys atra* or *P. nigricans*, on the other hand, the detrimental effect of *T. basicola* was greatly reduced.

The leaves of the plants in the original untreated old citrus soil were markedly chlorotic, exhibiting typical Fe-deficiency patterns. The fumigation treatment completely prevented development of the symptoms, but the inoculation of fumigated soil with *Thielaviopsis basicola* caused their reappearance. The fumigation treatment reduced leaf Ca and increased Mn, but inoculation of the fumigated soil with the various fungus species exerted little or no effect. Sodium tended to be higher in the plants making relatively poor growth. Leaf Fe-deficiency patterns were not correlated with total leaf Fe percentages (the leaves were prepared for analysis by the method recommended by Vanselow[2] and were analyzed for Fe three times and checked by a second analyst). No significant differences were found in percentages of leaf P, Mg, Cu, or Zn.

DISCUSSION

By fumigating the soil with propylene oxide, spreading to allow dissipation of the fumigant, and inoculating with pure cultures of fungi, it was possible to control the soil fungus populations to a surprising degree, although the soil was cropped to plants in 3-gallon pots in the greenhouse and no attempt was made to prevent contamination. Most species tested became established, and once

[2] Vanselow, A. P., and Liebig, G. F., Jr. Spectrochemical methods for the determination of minor elements in plants, waters, chemicals, and culture media. 1948. (Mimeographed) Univ. Calif. Office of Publs., Berkeley, Calif.

established, a particular species tended to resist establishment of other species for extended periods. Even after 8 months the fungus species in some soils apparently consisted only of those used for inoculation, but in other soils additional species were becoming established. Occasionally, certain forms, such as *Stemphylium piriforme*, *Epicoccum purpurascens*, *Pyrenochaeta* sp., and *Sclerotium* sp., failed to survive in one or more soils. Inability to compete with the bacterial population may have caused them to die out. The bacterial population of the soil rapidly returned after fumigation, and the forms occurring on dilution plates consisted largely of types producing fluorescent and pinpoint colonies.

The study demonstrated that the fungus population of the soil can vary tremendously without significantly influencing growth of citrus seedlings during a period of 8 months in the greenhouse. If any of the established fungus species retarded development of detrimental forms, the growing period was not long enough to reflect such action in total plant growth. Possibly a longer growing period or other species might have altered the results, or differences in fungus populations might affect growth of a second crop of seedlings in the same soil.

When a harmful fungus species became established, the types of fungi associated with it affected plant growth in some instances. *Thielaviopsis basicola*, under the conditions of this study, drastically reduced growth of the seedlings in two soils. When it was forced to compete with other fungi, such as *Penicillium nigricans* or *Stachybotrys atra*, growth retardation was less, but with species such as *P. funiculosum* or *Trichoderma viride* no improvement over *T. basicola* alone was evident.

Seedlings growing in old citrus Holtville silty clay loam and in the same soil fumigated and inoculated with *Thielaviopsis basicola* exhibited severe iron-chlorosis leaf patterns. This soil contains considerable lime, and the citrus leaf condition would ordinarily be referred to as lime-induced chlorosis. The fumigated noninoculated soil and soil from an adjacent field contained an equal amount of lime, but the leaves of seedlings growing in these soils were healthy and deep green. The total iron contents of the leaves of the green plants and of the chlorotic plants were not significantly different. The iron-chlorosis patterns of the seedlings were apparently associated with detrimental organisms.

Phytophthora citrophthora and *P. parasitica* are parasitic on citrus. They cause gummosis and root rot. Although they survived in the soil, they did not, in this experiment, significantly influence seedling growth. It is known, however, from extensive experiments and field observations, that they do parasitize and destroy citrus rootlets to a mild degree in soil of optimum moisture content and to a severe degree in waterlogged soil (4, 10).

SUMMARY

A greenhouse study was made of the influence of common soil fungi separately and in various combinations on growth of sweet orange seedlings in Yolo sandy loam and Holtville clay loam. Fumigation of the soil with propylene oxide, spreading to allow dissipation of the fumigant, and inoculation with spore suspensions of the desired fungi resulted in establishment in the soil of most of the

fungus species tested. Once established, a particular species tended to resist establishment of other species for extended periods.

The study demonstrated that the fungus population of the soil can vary tremendously without significantly influencing growth of citrus seedlings. Most species tested exerted little or no influence on growth of citrus seedlings. Under the conditions of the investigation, *Thielaviopsis basicola*, however, greatly reduced growth in two soils. When this organism was combined with other fungi, such as *Penicillium nigricans* or *Stachybotrys atra*, the reduction in growth was less, but with species such as *Penicillium funiculosum* or *Trichoderma viride*, no influence on the reduction in growth rate due to *T. basicola* alone was evident.

Thielaviopsis basicola caused strong iron-chlorosis leaf patterns on citrus seedlings in Holtville silty clay loam without changing the total iron content of the leaves.

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EFFECT OF SOIL REACTION ON UPTAKE OF NICKEL FROM A SERPENTINE SOIL

W. M. CROOKE

The Macaulay Institute, Aberdeen, Scotland[1]

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From time to time various reasons have been advanced to account for the infertility of serpentine soils, for example, alkalinity, low nitrate and phosphate content (7), an adverse Ca-Mg ratio (13), and the unsatisfactory nature of the soil microflora (12). Recently, using modern techniques, Vlamis and Jenny (18) concluded that the primary cause of this infertility is a very low soil Ca status, a hypothesis adequately confirmed by Martin, Vlamis, and Stice (14) in field experiments in which massive applications of $CaSO_4$ were used. Walker (19) found, however, that in a Californian serpentine soil poor growth still resulted after $CaSO_4$ application; investigation showed the soil to be deficient in Mo.

Robinson, Edgington, and Byers (17) were the first to propose that the infertility associated with certain types of serpentine soil could be attributed to their heavy-metal content. They studied Conowingo silt loam of Maryland and concluded that the levels of Ni and Cr present were high enough to be the primary cause of the infertility. Birrell and Wright (2) reached the same conclusion regarding a serpentine soil from New Caledonia. More recently workers in Japan (5) and Hawaii (3) commented on the high Ni content of their local soils, and Hunter and Vergnano (9) reported that the infertility of serpentine soils at Whitecairns in Aberdeenshire is due to toxic levels of Ni.

The area concerned in this report is about 9 miles north of Aberdeen and consists of a poorly drained basin about 4 miles long and 2 miles wide surrounded by low hills. The soils, which belong to the Leslie association (6) and are derived from a mixed drift in which serpentine predominates, are of two main types: a loam or peaty loam (pH 5.6–6.7) on the hill slopes ("hill soil"), and a peaty soil (pH 4.5–5.3) in the basin ("basin soil"). The P and K status of both of these soils is low, Ca is satisfactory and Mg high; the Mn status of the hill soils is low. The most striking feature of the soils is their very high acetic-acid-soluble and ammonium-acetate-soluble ("exchangeable") Ni contents (table 1).

Of the crops grown in the area, oats are most severely affected; the toxic symptoms produced consist of white necrotic tissue present as longitudinal stripes in the leaves, often accompanied by a diffuse chlorosis of younger leaves. The Ni content of fully expanded oat leaves from the area varies from 17–134 ppm. (basin soil) and 16–51 ppm. (hill soil). Field experiments showed liming to be the most satisfactory corrective treatment (9) and applications of gypsum ineffective.

[1] The author's present address is Chemistry Division, Science Service, Department of Agriculture, Ottawa, Ontario. The author wishes to thank Dr. E. G. Williams of the Macaulay Institute for his valuable suggestions and for his assistance in the preparation of the manuscript.

TABLE 1

Nickel content of soil

Type of Soil	Soluble in 0.5 N Acetic Acid	Soluble in Neutral N Ammonium Acetate
	ppm.	*ppm.*
Basin soil	114–289	26–61
Hill soil	49–403	22–49

This paper reports pot experiments which were designed to examine this effect of liming in more detail, together with results of laboratory experiments to measure the recovery of Ni added to soils of differing pH and to examine the form in which Ni occurs in the basin soils.

POT EXPERIMENTS

These experiments were carried out to assess the effect of liming on the uptake of Ni and on the toxicity symptoms produced in oats, with the hope of correlating the effects seen in the plants with changes in the level of soil Ni extractable by ammonium acetate.

The basin soil, because of its more satisfactory Mn status, was chosen for this work in preference to the hill soil. The levels of available nutrients in this soil (pH 4.8, loss on ignition 51 per cent) were determined by extracting 20 g. soil (<2 mm.) with 800 ml. 0.5 N acetic acid in an end-over-end shaker for 2 hours. The results were (as mg./100 g. soil): P_2O_5, 1.2; K_2O, 9.4; CaO, 430; and MgO, 68.5. A basal NPK[2] dressing was supplied to supplement the soil nutrients; a higher rate (twice basal) was also included to study its effect on the uptake of Ni. To improve drainage under these experimental conditions the soil was mixed with half its volume of coarse silica sand.

Two similar experiments were carried out; in the first, $CaCO_3$ was used to bring about the change in soil pH, and in the second Na_2CO_3 was used. The amounts added, as obtained by a preliminary laboratory study, were sufficient to raise the soil pH in 0.5-unit steps to an upper limit of 7. There were thus ten treatments in each series, and each treatment consisted of two 9-inch pots.

After the soils had been limed and fertilizers added, the pots were filled and watered for 7 days before the seeds were sown (100 oat seeds, variety "Victory," per pot). Before and after the experiment, the soil pH of each treatment and the level of exchangeable Ni in the soil were determined. After germination, plants were thinned to 80 per pot and allowed to grow for 35 days before being harvested. The experiment was conducted in a bird-proof cage during the summer.

In both series, nickel-toxic symptoms of moderate severity appeared in the control plants after about 10 days, but no symptoms appeared in any of the limed pots, although analysis showed the uptake of Ni was still appreciable. At harvest, yields of the two pots in each treatment were recorded, and after

[2] Per pot: N[as $(NH_4)_2SO_4$], 5 g.; P (as superphosphate), 6g; K (as KCl), 2.5 g.

TABLE 2

Soil and plant analyses for $CaCO_3$ and Na_2CO_3 series

Treatment No.	Final Soil pH		Exch. Ni in Soil		Fresh Yield per 100 Plants		Concentration in Leaf Dry Matter				Necrotic* Symptoms	
							Fe		Ni			
	$CaCO_3$ series	Na_2CO_3 series	$CaCO_3$ series	Na_2CO_3 series	$CaCO_3$ series	Na_2CO_3 series	$CaCO_3$ series		Na_2CO_3 series		$CaCO_3$ series	Na_2CO_3 series
			ppm.	*ppm.*	*g.*	*g.*	*ppm.*		*ppm.*			
Low fertilizer dressing												
1	5.2	4.8	55	40	64.8	73.0	58	117	188	144	M	M
2	5.7	5.7	52	30	74.4	99.2	56	122	102	109	0	0
3	6.4	6.2	39	32	110.7	93.9	63	107	98	79	0	0
4	6.8	6.0	31	24	92.3	74.5	80	103	75	49	0	0
5	7.1	6.8	26	24	92.4	83.4	104	92	77	40	0	0
High fertilizer dressing												
6	5.1	4.7	54	41	87.2	100.2	65	125	185	113	M	M
7	5.5	5.4	46	39	109.6	87.5	137	115	128	96	0	0
8	6.0	5.9	42	38	102.4	95.0	92	115	98	84	0	0
9	6.7	6.6	28	35	109.4	76.7	76	115	80	58	0	0
10	7.0	7.2	25	21	128.5	76.7	84	96	75	48	0	0

* On scale: high (H), medium (M), low (L).

drying overnight at 80°C. fully expanded leaves were analyzed for Ni and Fe contents. The mean results are recorded in table 2.

LABORATORY EXPERIMENTS

Recovery of Ni from limed soils

While the pot experiments were being conducted, the recovery of added nickel from soils of various pH values was studied. The soils were from plots in a long-term liming experiment on a granitic soil which probably contained less than 2 ppm. acetic-acid-soluble Ni (15). Four experiments, which differed in detail only, were carried out. In the first, the soils used had received (A) no lime, (B) 17.5 cwt., (C) 35 cwt., and (D) 52.5 cwt. CaO per acre. In the second and third experiments, soil A was limed with either $CaCO_3$ or Na_2CO_3 to about pH 7, in 0.5-unit steps, before the addition of Ni. Finally, the effect of increased Ca status (by use of gypsum) on the recovery of Ni was tested in the fourth experiment.

In each case 4 mg. Ni in solution was added to 20 g. air-dried soil (<2 mm.) together with enough water to bring the soil to 30 per cent moisture capacity. The soils were stored moist for 10 days before being air-dried and leached with neutral *N* ammonium acetate; the exchangeable bases and Ni were then determined in the leachate. The actual pH obtained was measured in a series of controls carried through the same procedure but without added Ni. Each treatment was set up in duplicate. Agreement between replicates was good (mean

TABLE 3

Recovery of nickel from limed soils

Soil pH	Ca in Soil me./100 g.	Ni Recovered
Experiment 1		
A* 5.2	2.85	59
B 5.5	4.20	55
C 5.8	5.40	54
D 6.2	8.40	41
Experiment 2†		
5.2	3.00	52
5.7	5.40	48
6.2	7.65	40
6.6	10.35	29
6.9	13.65	21
7.0	19.65	16
Experiment 3‡		
5.3	2.70	50
5.9	2.70	46
6.2	2.70	45
6.7	2.70	43
Experiment 4§		
5.3	2.40	47
4.8	4.80	48
4.7	6.90	51
4.6	9.90	52
4.6	12.30	50
4.6	16.50	53

* CaO (cwt./A.) added to soils: A, none; B, 17.5; C, 35; D, 52.5.
† Soil A on addition of 0, 30, 60, 100, 140, 210 mg. $CaCO_3$ per 20g. soil.
‡ Soil A on addition of 0, 10, 20, 40 mg. Na_2CO_3 per 20g. soil.
§ Soil A on addition of 0, 41, 82, 136, 190, 286 mg. $CaSO_4$ per 20g. soil.

values are given in table 3) but since the results obtained for K and Mg varied only slightly with pH changes, they have been omitted from the reported data.

Form of Ni in the basin soils

Although in the serpentine area at Whitecairns the highest acetic-acid-soluble Ni figures recorded by Vergnano[3] were for mineral soils on the hill slopes, the toxic symptoms and uptake of Ni were highest in plants from the basin soils.

[3] Vergnano, O. Physiological aspects of the nickel-soil-plant relationship. 1951. (Unpublished Ph.D. thesis. University of Aberdeen.)

Clearly pH difference between the two soils was the main factor involved, although the form in which Ni occurred in the basin soils might affect the amount of Ni absorbed by plants.

In this connection, the literature makes it clear that trace metals, especially Cu and Mn, added to peaty soils are often held so firmly by the soil that the usual soil extractants will not displace them. The inference is that metallo-organic complexes have been formed (11) which have the effect of "fixing" the metal. Heintze and Mann (8) suggested that the unavailability of Mn in neutral and alkaline soils may be due to a mechanism of this sort. Moreover, they found that only a very small part of the Mn added to such soils could be recovered by extraction with ammonium acetate, although recovery was markedly increased by addition of low concentrations of Cu, Cd, Zn, or Ni salts to the extractant.

Vergnano's results and the foregoing considerations suggested that part of the Ni in the basin soil might be associated with the soil organic matter as a complex from which Ni was not readily displaced by either acetic acid or ammonium acetate, although in contrast to the Cu or Mn soil complexes, the Ni in this complex appeared to be freely available to plants.

To test this hypothesis, duplicate 20-g. lots of basin soil (pH 4.6 and total Ni content 1000 ppm.) were extracted overnight with the following extractants: (*a*) water, (*b*) 0.5 *N* acetic acid, (*c*) aqueous 1 per cent $ZnSO_4$, (*d*) 1 per cent $ZnSO_4$ in 0.5 *N* acetic acid, and (*e*) 0.5 per cent K_2SO_4. The mean values obtained are given in table 4.

TABLE 4

Nickel extracted from Whitecairns basin soil

Extractant	Nickel in Soil
	ppm.
Water	7.2
Acetic acid	219
$ZnSO_4$	294
$ZnSO_4$ in acetic acid	330
K_2SO_4	17

TABLE 5

Effect of soil organic matter destruction on solubility of soil nickel

Sample No.	Nickel in Soil		
	Filtrate	Mineral fraction*	Total
	ppm.	*ppm.*	*ppm.*
1	730	87	817
2	760	80	840
3	739	34	773
4	758	73	831

* Extractants for mineral fraction: samples 1 and 2, 0.5*N* acetic acid; sample 3, 1 per cent aqueous $ZnSO_4$; sample 4, $ZnSO_4$ in 0.5*N* acetic acid.

An approximate measure of the amount of Ni associated with the organic fraction of the basin soil was obtained by destruction with hydrogen peroxide of the organic matter in four 20-g. samples. After peroxide treatment the soil suspension was filtered and Ni determined in the filtrate. The mineral fraction that remained was extracted overnight with: (samples 1 and 2) 0.5 *N* acetic acid; (sample 3) 1 per cent aqueous $ZnSO_4$; and (sample 4) $ZnSO_4$ in 0.5 *N* acetic acid. The results shown in table 5 were obtained.

The increase in Ni extracted from the basin soil by $ZnSO_4$, in either water or acetic acid, over that extracted by acetic acid alone, is noteworthy. The low amount of Ni extracted by K_2SO_4 suggests it is unlikely that the effect of Zn is due solely to mass action. It would appear that Zn is displacing Ni associated with the soil organic matter in a form not readily extractable by acetic acid.

Destruction of the organic matter freed much more Ni than did displacement by Zn, and in fact, the total figure (filtrate plus mineral fraction) closely approached the total soil content. The possibility that organic acids may have attacked the mineral fraction during the prolonged peroxidation should not be overlooked.

DISCUSSION

The main feature of the results of the pot experiment with the basin soil was that, irrespective of whether $CaCO_3$ or Na_2CO_3 was employed, the uptake of Ni by the plants and the amounts of Ni extracted fell as the pH of the soil increased. It would appear, therefore, that change in soil pH rather than improved Ca status is the dominant factor. This conclusion is supported by the fact that Na_2CO_3 tends on the whole to be appreciably more effective than $CaCO_3$. The mechanism of the pH effect is not clear, but it seems highly probable that a change in the form of the soil Ni is involved. Little information exists in the literature on the categories of soil Ni, but Krotov (10) noted that Ni was precipitated in soils at a pH between 6 and 7, while Oertel, Prescott, and Stephens (16) found that Ni uptake by clover was greatest from soils of acid reaction.

It is interesting to note that, at each pH level, plants in the Na_2CO_3 series absorbed less Ni than did those in the $CaCO_3$ series, and that this lowered uptake of Ni was accompanied by an increased absorption of Fe. This agrees with the results of Crooke, Hunter, and Vergnano (4), who found in sand-culture experiments that increased supply of either element reduced absorption of the other.

In support of the validity of the results obtained in the laboratory with the granitic soil is the close agreement between the values for Ni recovery from soils limed in the field and those limed in the laboratory. These results, in contrast to those obtained with the basin soil, show $CaCO_3$ to be considerably more effective than Na_2CO_3 in reducing the recovery of added Ni. In this case, therefore, the results tend to suggest that Ca status may play some part in affecting recovery, but against this theory, is the fact that addition of $CaSO_4$ to the unlimed soil had little effect on the recovery of Ni in spite of the marked changes in soil Ca content. In keeping with the decreasing pH, the higher additions of

$CaSO_4$ actually caused an increase in recovery. Since the effect of Ca on recovery may vary, depending on the pH range under consideration, further work is necessary to clarify this point.

The effect of liming on the uptake of trace-element cations, particularly Mn under acid soil conditions, has received considerable attention in the past. Most reports have noted a reduction in exchangeable Mn on liming, which resulted in a reduced absorption of the element by plants. Askew and Dixon (1) found that liming reduced the uptake of Co by pasture species. The results obtained here for Ni are in general agreement with the findings for other trace cations.

On the basis of earlier work and the present limited study of the basin soil, there appears to be some justification for concluding that forms of Ni exist in this soil which, although not extractable by acetic acid, are still available to oat plants. Addition of $ZnSO_4$ to the acetic acid solution appears to displace some of this Ni, and destruction of the soil organic matter releases Ni in amounts that approximate the total soil content. Taken in conjunction with the contrasting behavior between the basin soil and the granitic soil, these considerations really suggest that although soil pH is almost certainly an important factor in governing the availability of trace cations in all soils, its effect may be considerably modified by other soil characteristics, particularly organic matter content in relation to possible complex formation.

SUMMARY

In pot experiments with a serpentine soil, increase in soil pH, whether produced by $CaCO_3$ or Na_2CO_3, was found to reduce Ni extractable by ammonium acetate and also that absorbed by oat plants.

Laboratory studies were made of the recovery of Ni added to a granitic soil limed by either $CaCO_3$ or Na_2CO_3. Increase in soil pH was found to reduce recovery.

The results of the experiments suggest that the reduction in toxicity symptoms and Ni absorption produced by liming of these serpentine soils in the field depends on a reduction in available Ni due to change in soil pH, rather than on the improved Ca status of the soil.

In a peaty serpentine soil, there are indications that part of the Ni exists as a complex with the soil organic matter.

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ACIDIC PROPERTIES OF QUARTZ

J. REX GOATES AND KENNETH ANDERSON

Brigham Young University[1]

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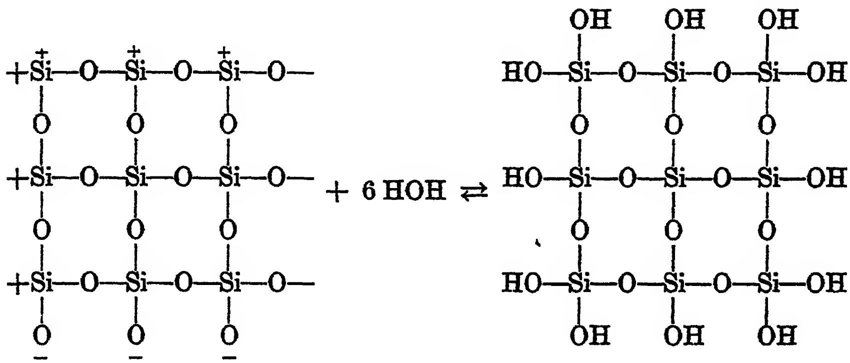
The structures of the various crystalline forms of silica, which were discussed by Wells (8), are three-dimensional frameworks of silica tetrahedrons linked together in such a way that every oxygen is shared by two tetrahedrons. In such structures, therefore, every oxygen is connected to two silicons, and each silicon to four oxygens. A representation of this bonding (not the structure) is shown in reaction (*1*). This reaction also shows how "broken valence bonds"



(*1*)

on the surface of silica crystals can give rise to acidic sites. The breaking of the crystal through any plane is the breaking of Si-O bonds only. When this happens, the oxygen, since it is more electronegative than the silicon, would be expected to retain the pair of electrons that made up the bond, and the silicon to acquire a positive charge. Thus in presence of an ionizable solvent such as water, the negative charge on the oxygen would be neutralized by H^+, and the positive charge on the silicon would be neutralized by OH^-. Although of different origin, once these monoprotic groups are formed, they react with a base in the same way. These groups should represent the major part of the titrable acidity of silica. Other acidic sites might also be predicted from the model, such as the diprotic groups shown in figure 1 attached to silicons exposed at the corners of crystals.

MATERIALS AND METHODS

Titrations of finely ground, electrodialyzed quartz were made in (*a*) absolute ethanol solutions with $NaOC_2H_5$, and (*b*) water solutions with NaOH. The organic solvent was used in the first experiments to minimize the solubility of silica in the highly basic solutions that are necessary to reach an equivalence point in the titration of quartz.

[1] This investigation was supported by a grant from the National Science Foundation.

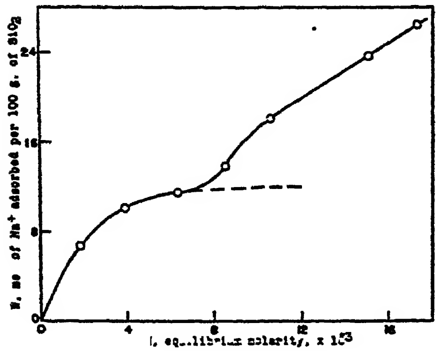


FIG. 1

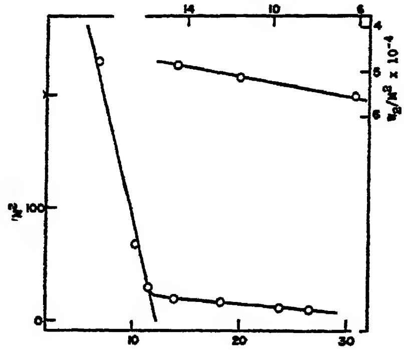


FIG. 2

FIG. 1. ADSORPTION OF Na^+ ON QUARTZ IN ETHANOL

FIG. 2. REACTION OF $NaOC_2H_5$ WITH QUARTZ; PLOTTED ACCORDING TO EQUATION (2)

The silica sample was prepared from 325-mesh flint.[2] It was ground wet in a porcelain ball mill with smooth flint rocks. Particles in the size range of 100–300 mμ were separated from the bulk sample by means of a Sharples supercentrifuge; they were then electrodialyzed and washed successively with ethanol, acetone, and benzene. The sample was dried at 70°C. in a vacuum of about 25 μ.

One-half-gram samples of the quartz powder were weighed into 50-ml. steel centrifuge tubes, and varying amounts of absolute ethanol and $NaOC_2H_5$ in ethanol solution were added to each. The total volume of liquid added to each tube was 40 ml. The tubes were capped and rocked gently in a 25 ± 0.02°C. water bath for 18 hours, after which the suspensions were centrifuged, and the decantate was analyzed for Na^- concentration with a Beckman flame spectrophotometer. Analyses were made in duplicate and were reproducible to within 1 per cent.

The procedure for the titrations in water solutions was similar, except that after the suspensions had equilibrated, their pH was determined with a glass electrode, and their Na^+ activity was determined by clay membrane electrodes of the type described by Marshall (4, 5, 6, 7). The concentration of the silica in these suspensions was 0.55 per cent.

RESULTS AND DISCUSSION

The titration data for the ethanol system are recorded in table 1. The adsorption isotherm for Na^+ on the quartz sample is shown in figure 1. Since electrical neutrality will be maintained, the ordinate of figure 1 might also be considered a measure of the $C_2H_5O^-$ that has reacted. The inflection occurring near the equilibrium concentration of 8×10^{-3} M suggests the presence of two types of

[2] Purchased from Harshaw Scientific Co.

acid sites. The presence of the two types is confirmed by a plot (fig. 2) of the data according to the Langmuir-type equation:

$$W/m^2 = K'W - K'W_0 \qquad (2)$$

where W is the amount of $NaOC_2H_5$ reacted, in me. per 100 g. of quartz; W_0 is the total titrable acidity of the quartz, measured in me. per 100 g.; m is the equilibrium concentration of $NaOC_2H_5$; and K' is an apparent equilibrium constant. An earlier paper (3) gives the derivation and discusses further the application of equation (*2*).

The steep line part of the curve on the left side of figure 2 (read left side ordinate and bottom abcissa) shows the presence of one type of acid site; the change to a much smaller slope in the latter part of the curve indicates a second, weaker types of acid site. Using the value of K' of the first reaction, obtained from the slope of the steep line portion, we subtracted the effect of the first reaction from the total to obtain the amount of $NaOC_2H_5$ reacted in the second-type reaction. These data are plotted on the right side of figure 2 (read right side ordinate and top abcissa). The constants of equation (*2*) are recorded in table 2.

The values of K' show that the acids are very weak. The K' value for the titration of the stronger of these two sites is almost an order of magnitude smaller than that for the titration of H^+-clays (3), and the weaker site on silica is more than three orders of magnitude weaker than that for the H^+-clays.

The relative concentrations of the two types of sites indicate that the breaking of Si-O bonds along flat surfaces produces the weaker, more numerous, second-

TABLE 1

Titration of dialyzed silica with $NaOC_2H_5$ in C_2H_5OH

$NaOC_2H_5$ Added Per 100 g. Quartz	Equilibrium Concentration	Na^+ Adsorbed Per 100 g. Quartz
me.	$M \times 10^{-3}$	*me.*
0.0	0.00	0.0
20.6	1.72	6.8
41.2	3.88	10.2
61.8	6.28	11.5
82.4	8.56	13.9
103.0	10.60	18.2
144.2	15.06	23.7
164.8	17.23	26.6

TABLE 2

Constants of equation (1) *for the titration of quartz with $NaOC_2H_5$ in C_2H_5OH*

Acid Site	K'	W_0
		me./100 g.
First type...	4.0×10^5	12.2
Second type...	8.9×10^2	68.9

TABLE 3

Titration of dialyzed silica with NaOH in water

NaOH Added Per 100 g. SiO_2	Activity of Na^+ at Equilibrium	Na^+ Adsorbed per 100 g. SiO_2	pH
me.	$a \times 10^{-5}$	*me.*	
0.00	—	—	5.89
1.92	5.7	0.9	7.32
3.84	7.6	2.5	8.02
5.77	8.7	4.2	8.52
7.69	10.0	5.9	8.88
9.61	11.5	7.5	9.20
11.53	14.0	9.0	9.43
13.55	18.0	10.1	9.55
15.37	26.0	10.6	9.68

type sites. The smaller number of more acidic-type sites may be those at the corners of the crystals where diprotic silicic acids are shown in the model. If the model is correct, a third-type site of the same surface concentration as that of the first type would also be present. One would predict from the electronegativities of the elements attached to the central silicon atom that the order of increasing acidity of the three acids would be first ionization of a diprotic site > monoprotic site > second ionization of a diprotic site. In view of the generalization that a second ionization constant of a diprotic acid is usually of the order of 10^{-5} of a first ionization, K' for the third-type site could be expected to be about unity. That is, to titrate only one-half of these sites, the equilibrium concentration of the base would have to be about 1 M, or far beyond the range of the titration made in this study. We were unable, therefore, to detect the presence of a third-type site.

Table 3 records the titration data for the water system. Figure 3 shows the shape of the pH and pNa (negative logarithm of Na^+ activity) curves. In figure 4 the data were plotted according to an equation of the type developed by Cook *et al.* (1, 2) for describing titration data of clay minerals. For the titration of silica the development of this equation is as follows:

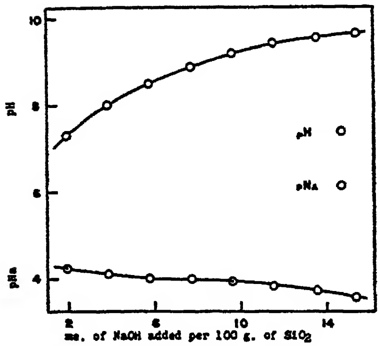
Let $(XH)_1$ represent acid site type 1; and $(XH)_2$, acid site type 2. The equilibrium equations involved in the titrations are:

$$(XH)_1 \rightleftarrows X^- + H^+ \tag{3}$$

$$(XH)_2 \rightleftarrows X^- + H^+ \tag{4}$$

$$X^- + Na^+ \rightleftarrows X^-\text{—}Na^+ \tag{5}$$

The symbol X^-—Na^+ represents Na^+ adsorbed by the charged site X^-. Once a site has ionized, no distinction needs to be made as to the origin of the charge; hence, subscripts are omitted from X^-.



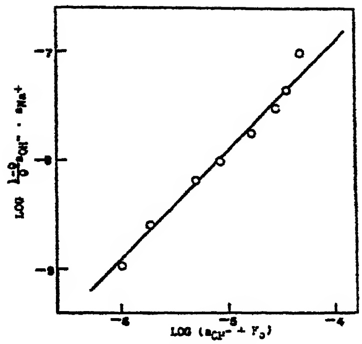


FIG. 3 FIG. 4

FIG. 3. TITRATION OF QUARTZ WITH NaOH

FIG. 4. PLOT OF THE LOGARITHM OF EQUATION (*10*) FOR THE TITRATION OF QUARTZ WITH NaOH

The equilibrium constants for these equations are:

$$K_1 = \gamma_1[X^-]a_{H^+}/\gamma_2[(XH)_1] \quad (6)$$

$$K_2 = \gamma_1[X^-]a_{H^+}/\gamma_3[(XH)_2] \quad (7)$$

$$K_3 = \gamma_4[X^- \text{—} Na^+]/\gamma_1[X^-]a_{Na^+} \quad (8)$$

The a's are activities, the brackets represent surface concentrations, and the γ's are the appropriate activity coefficients.

The surface site balance equation for the system is:

$$[S_0] = [X^- \text{—} Na^+] + [X^-] + [(XH)_1] + [(XH)_2] \quad (9)$$

The symbol S_0 is used to designate the total number of possible sites.

Simultaneous solution of equations (*6*), (*7*), (*8*), and (*9*), and substitution of the symbol θ for the fraction of S_0 adsorbing Na^+ give the Cook *et al.* equation:

$$\frac{1-\theta}{\theta} a_{Na^+} a_{OH^-} = K_3'(a_{OH^-} + K_0) \quad (10)$$

K_3' is equal to $\gamma_1 K_3/\gamma_4$, and K_0 for the silica titration is $(K_W\gamma_1/K_1\gamma_2) + (K_W\gamma_1/K_2\gamma_3)$, where K_W is the ion product constant of water.

Using a value of S_0 (needed to calculate θ) of 80 me. per 100 g. (the sum of the acidic sites found in the alcohol study), we found $K_3' = 1.23 \times 10^3$, and $K_0 = 1 \times 10^{-7}$. K_3' is an approximation of the equilibrium constant of equation (*5*). Since this represents diffuse double-layer adsorption, the value obtained for this constant would both be expected to be and is very close to those found in clay mineral studies (1, 2). K_0 values for clay minerals, on the other hand, are three to four orders of magnitude smaller than that obtained in this study, which indicates that the origin of the negative charges on the clays is quite different from that of silica.

SUMMARY

Titration studies of finely ground quartz were made in absolute ethanol with $NaOC_2H_5$ as the base. Two types of weakly acidic sites were observed. The data were interpreted in terms of a "residual valence bond" model.

Titration studies of quartz in water suspensions with NaOH as the base were also made. The data include measurements of the Na^+ activity, as well as pH, of the suspensions at equilibrium. These data were adequately described by a form of the Cook *et al.* equation. The constants of this equation were determined and compared with similar data for clay minerals.

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HYDRAULIC CONDUCTIVITY IN LARGE CHANNELS AS DETERMINED BY AN ELECTRIC ANALOG

W. D. KEMPER AND J. F. LUTZ

North Carolina State College[1]

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One of the problems in measuring hydraulic conductivity of soils is how to evaluate the contribution of highly conductive channels to total conductivity. This problem is particularly acute when measurements must be made on undisturbed core samples. Almost invariably, in taking these samples large channels, such as cracks, old root holes, and crawfish holes, are avoided even though such channels often provide an appreciable part of the total hydraulic conductivity. In the experiment reported here, an electric analog was set up to measure the contribution of such channels to the total hydraulic conductivity of an otherwise homogeneous soil.

THEORY AND CONSTRUCTION OF THE ANALOG

The conductivity of channels approximately 0.5 cm. in diameter is very large in relation to that of the surrounding soil. The electric analog (fig. 1) was constructed on the basis that the same relationship will also hold for the electrical conductivity of lengths of polished copper wire suspended in an agar gel.

The frame was built of two ½-inch "Flexaframe" rods (*A*), and four "Flexaframe" couplings (*B*). Each coupling held a lucite rod (*C*) 4 inches long and ½ inch in diameter. These rods were wired to sheets of varnished plywood (*D*) ¼ inch thick. Copper screen was stapled to the inside faces of the two sheets of plywood, covering them completely. The assembly was then placed in an enameled pan, and the edges of the plywood and attached copper screen were cut to fit flush against the sides and the bottom of the pan.

PROCEDURE

Thirty grams of dry agar was added to 3 liters of water. The mixture was heated for 3 hours at 95°C, and the resulting suspension was stirred while it cooled. A finely granular agar gel was obtained, which after room temperature was reached had little, if any, tendency to aggregate into large units. This granular gel was then poured into the enameled pan and the copper screen electrodes were inserted 22 cm. apart. There was 127.5 sq. cm. of copper screen electrode in contact with the agar at each surface (*D*). Thus the total volume of agar gel between the electrodes was 2805 cc.

A conductivity bridge was then attached to the copper screen electrodes, and the conductivity of the agar gel was measured. Subsequently, the con-

[1] Paper 672 of the Journal Series, from the department of agronomy, North Carolina Agricultural Experiment Station, Raleigh. This investigation was conducted while the senior author was a graduate assistant at North Carolina State College, Raleigh; he is now at Colorado A. and M., Fort Collins.

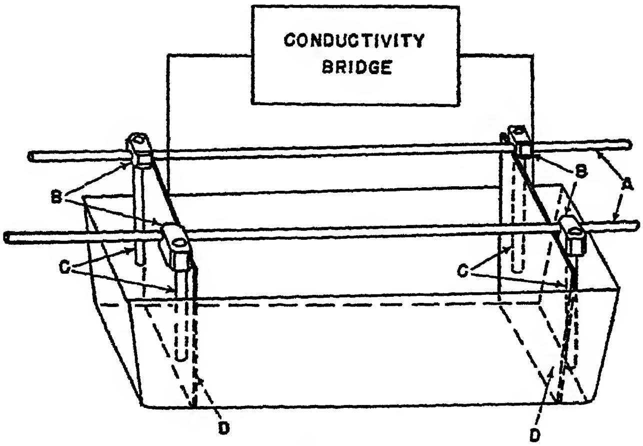

FIG. 1. SCHEMATIC DIAGRAM OF THE ELECTRIC ANALOG

ductivity of the agar was measured when it contained the following amounts of 0.015 cm. diameter copper wire: (*a*) 40, 80, and 160 pieces 2.5 cm. long; (*b*) 10, 20, 40, and 80 pieces 5 cm. long; and (*c*) 10, 20, and 40 pieces 10 cm. long. From time to time the conductivity of the agar suspension itself was checked to determine whether it had been changed by temperature variations or by contamination.

Since the contribution of the copper wire to the conductivity is a function of its random distribution and orientation, five readings were taken for each copper wire "treatment." Between readings the agar and wires were agitated with L-shaped stirring rods to obtain different distributions and orientations.

RESULTS AND DISCUSSION

The percentage increase in conductivity caused by addition of the various amounts and lengths of wire to the agar suspension is plotted in figure 2. The values shown are the averages of five readings, with the 5 per cent confidence limits indicated. From these amounts or "concentrations" of wire, the percentage increase in conductivity appears to be a linear function of the number of pieces of wire and, therefore, of the total length of wire.

The regression coefficients of the increase in conductivity on the concentration (expressed in centimeters per cubic centimeter) of added wire were calculated for each length of wire used. Figure 3 shows the logarithms of the regression coefficients (b) plotted against the logarithms of the lengths of the pieces of wire (L), with the 5 per cent confidence limits indicated for each point. The equation of the resultant straight line with a slope of 2.0 is $\log_{10}b = 2.0 \log_{10}L + 0.66$, in which b is the regression coefficient and L the length of the pieces of wire. Taking this relationship out of its logarithmic form we have:

$$b = 4.57\, L^2 \qquad (1)$$

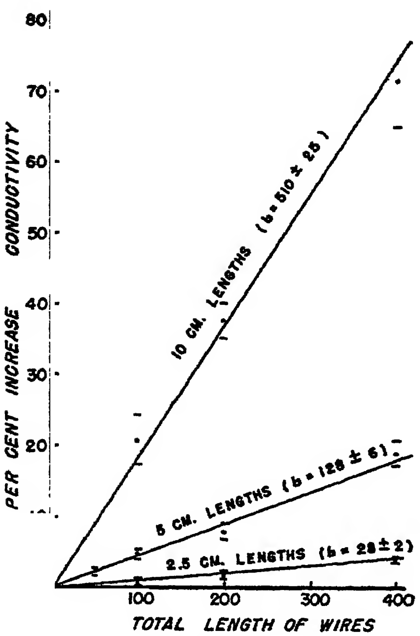

Fig. 2

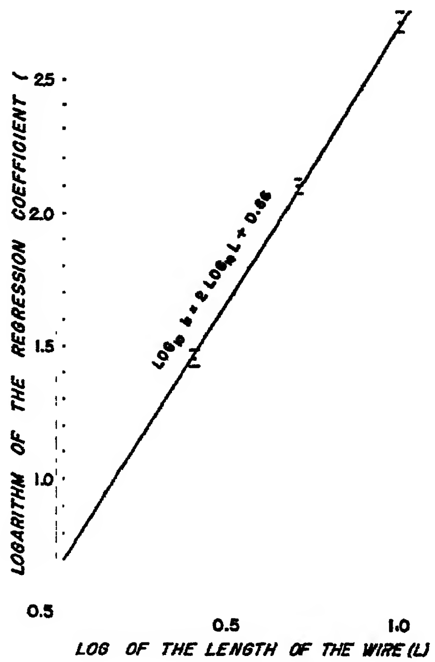

Fig. 3

Fig. 2. Effect of Amount of Wire Added on the Conductivity of the System
Fig. 3. Effect of Lengths of Pieces of Wire on the Regression Coefficient

In this equation b is the percentage increase in conductivity per unit length of wire added per unit volume.

If n equals the number of pieces of wire per unit volume, then nL represents the length of wire added per unit volume. The percentage increase in conductivity (C) of the system with reference to the system containing no wire can thus be expressed as:

$$C = bnL \tag{2}$$

Substituting in equation 2 the value for b from equation 1 gives

$$C = 4.57\, nL^3 \tag{3}$$

Equation 3 represents an empirical relationship derived from experimental data. The ranges of wire concentration are fairly low, and it is improbable that this simple relationship would hold at high concentrations. The equation may be considered, however, to show the approximate relationship of the number of root, crawfish, or worm channels per unit volume; the average length of these channels; and their contribution to the over-all hydraulic conductivity of the soil. The equation will be most accurate when the channels are large in diameter,

equal in length, homogeneous in distribution, random in orientation, and not too great in number.

SUMMARY

Data from an electric analog were used to develop an equation relating the number and length of highly conductive channels to their contribution to overall hydraulic conductivity.

PHYSICAL, CHEMICAL, AND MINERALOGICAL PROPERTIES OF BROWN PODZOLIC SOILS IN SOUTHERN NEW ENGLAND: PAXTON AND MERRIMAC SERIES

TSUNEO TAMURA

Connecticut Agricultural Experiment Station[1]

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The properties of two representative soils of the brown podzolic group were investigated to obtain a better understanding of the character of soils classified as brown podzolic, and thus to make the possible use of such soils more efficient and productive. Both of the soils studied, Paxton fine sandy loam and Merrimac fine sandy loam, are important agriculturally. In the eastern and western highlands of Connecticut and Massachusetts, Paxton is used primarily for hay production, pasture, and corn. In the Connecticut valley, Merrimac is the most important soil for the growing of cigar tobacco.

Paxton fine sandy loam is developed on firm schistose and granitic Wisconsin till, and Merrimac fine sandy loam from glacial outwash, principally granite, gneiss, and schist. The physiography, drainage, geology, parent material, climate, vegetation, and some other characteristics of these soils have been presented elsewhere (9, 10). Here we shall be concerned with their physical, chemical, and mineralogical properties.

Since the profile description for the Merrimac fine sandy loam, sampled at Windsor, Connecticut, has been published (1), only a brief resumé for easy reference is included here; the Paxton profile was obtained from the agronomy plots of the University of Connecticut, Storrs. On the basis of field studies (12), these profiles are believed to represent the modal properties of brown podzolic soils as developed from their respective parent materials prevalent in Connecticut.

PAXTON FINE SANDY LOAM[2]

Location: Agronomy plots, University of Connecticut, Storrs; Plot G3, southwest corner in roadway (pit).
Topography: Drumloidal hill; slope 2 per cent.
Vegetation: Hay.

[1] Contribution from the department of soils, The Connecticut Agricultural Experiment Station, New Haven. Grateful acknowledgment is made to C. L. W. Swanson of this department and W. H. Lyford, Soil Conservation Service, for comments and criticisms. Appreciation is also expressed to D. B. Downs, R. M. Hanna, and G. Talvenheimo for some of the analytical data.

[2] For many years this soil was correlated as Charlton, on the basis of an early soil map by Morgan (9), but a recent detailed survey by A. E. Shearin, Soil Conservation Service, showed the soil to be within the range of the Paxton series. The structural notation of subangular blocky is appropriate for fragment or clod description; the aggregates lack ped characteristics.

Drainage: Well drained; surface runoff slow; internal drainage moderate to slow.
Parent material: Firm schistose and granitic Wisconsin till.
Use: Hay production and pasture.

Soil profile description

Horizon	*Depth*	*Description*
A_p	0 to 8 inches	Very dark grayish brown (10 YR 3/10)[3] fine sandy loam, firm in place and friable when removed; granular structure 0 to 3 inches changing into medium subangular blocky at 3 to 8 inches which breaks down into a granular mass when crushed. Worm channels present throughout horizon. Several yellowish brown subsoil fragments incorporated in the lower part. No evidence of grit, but small stone fragments 1 cm. in diameter abundant. Grass roots numerous. pH 5.8.
B_{21}	8 to 14 inches	Yellowish brown (10 YR 5/8) fine sandy loam, very weak medium subangular blocky structure 8 to 11½ inches; 11½ to 14 inches very weak coarse subangular blocky. From 8 to 10½ inches considerable incorporation of organic matter in worm channels; below 10½ inches worm channels seem to be absent, but root channels are abundant. Rock composition is variable; about 5–10 per cent of the fragments are chert and quartz from gneissic and granitic rocks, most of them very angular; the larger fragments originate from hornblende and garnet-chlorite varieties of schists and are in a moderate state of weathering. The larger fragments of schist are oriented at random. pH 5.9.
B_{22}	14 to 19 inches	Light olive-brown (2.5 Y 5/6) fine sandy loam, very weak coarse subangular blocky structure; firm in place and friable when removed. Rock fragments of schist, diabase, and granite make up about 5–10 per cent of the coarse materials. Many roots extend to this horizon but few penetrate deeper. pH 6.0.
B_3	19 to 25 inches	Olive (5 Y 5/4) gritty fine sandy loam, more compact in place than the overlying horizon, but friable when removed. Rock fragments of same composition as in B_{22} make up about 5–10 per cent of the materials. Virtually no roots penetrate deeper than 25 inches. pH 6.0.
C_m	25 to 45 inches	Olive-gray (5 Y 5/2) compact fine sandy loam. Percentage of gravel up to 2 cm. in diameter (25 per cent by volume) considerably higher than in overlying horizon. This material is firm till, which at the time of sampling was thought to be less compact than the Paxton till but later was found to be just as compact. Most of the flat rocks and boulders lie horizontally, but the smaller rock fragments are randomly oriented. The systematic orientation of boulders indicates some compression of these materials while the till was still friable. The sharp difference between the B and C horizons suggests differential depositional environments rather than differential weathering. Both fresh and altered materials make up the material below 25 inches. Drainage conditions below 30 inches are poor and some mottling shows up in places. Boulders and stones are not uniformly distributed within the finer materials. pH 6.2.

[3] Munsell color notation of moist soil.

Horizon	*Depth*	*Description*
D_1	45 to 70 inches	Olive (5 Y 5/4) fine sandy loam. This material is different in appearance from the overlying horizon. It is loose and crumbles readily into medium subangular blocky fragments. The general trend of structure is toward platiness but not regularly so; a discontinuity in the structural pattern suggests some kind of disturbance after the original platy structure was developed. Very peculiar forms of dark brown rusty spots occur as circular lenses 1 to 3 mm. in diameter and as shreds between irregular plates; these were found to be weathered garnets. This intricate pattern of weathered garnets is imprinted on stones. Many micaceous mineral fragments (muscovite and chlorite) were noticed in the gravels of this material. The water table was found at 70 inches. pH 6.4.
D_2	70 to 85 inches	Sample taken with an auger. pH 6.2.
D_3	85 to 91 inches	Sample taken with an auger. pH 6.4.

MERRIMAC FINE SANDY LOAM

Soil profile description

Horizon	*Depth*	*Description*
A_{11}	0 to 2 inches	Very dark grayish brown (10 YR 3/2) fine sandy loam. An incipient gray layer is present in places. pH 3.7; very rapid permeability.
A_{12}	2 to 3 inches	Transition layer of interfingering A_{11} and A_p. pH 4.3.
A_p	3 to 8 inches	Dark yellowish brown (10 YR 3/4) fine sandy loam. A weak platy structure has developed in the lower part. pH 4.6; rapid permeability.
B_{22}	8 to 12 inches	Strong brown (7.5 YR 5/6– 5/8) fine sandy loam, very friable. pH 4.5; moderate permeability.
B_{23}	12 to 20 inches	Strong brown (7.5 YR 5/6–5/8) to yellowish brown (10 YR 5/6) fine sandy loam. Massive in place but crushes into soft crumbs. pH 4.6; moderate permeability.
D_1	20 to 26 inches	Yellowish-brown (10 YR 5/6) loamy coarse sand. pH 4.8; moderate permeability.
D_2	26 to 33 inches	Yellowish brown (10 YR 5/6) fine sand. pH 4.9; moderately rapid permeability.
D_2	33 to 70 inches	Brown (10 YR 5/3) stratified coarse sand and fine gravels. pH 4.9; very rapid permeability.

EXPERIMENTAL TECHNIQUES

Mechanical analyses were made by the Agricultural Research Service, Beltsville, Maryland, according to the method of Kilmer and Alexander (8). The elemental analysis procedure was developed by Corey and Jackson (4). The x-ray equipment consisted of a Norelco Geiger Counter Spectrometer for oriented samples and a 114.59 mm. diameter camera for unoriented specimens. Differential thermograms were made by use of facilities made available by the geology department of Yale University. Cation-exchange capacities of the clays were determined by Peech's method (10), and free iron oxide content of the clays by Deb's method (5). Total free oxides were determined on the <2-mm. particles by Jeffries' method (7). Bulk density and porosity were measured by the proce-

TABLE 1

Mechanical analysis of Paxton and Merrimac soils

Horizon	Depth	Acidity	Organic Carbon	Size Class and Diameter of Particles							
				Very coarse sand, 2–1 mm.	Coarse sand, 1–0.5 mm.	Medium sand, 0.5–0.25 mm.	Fine sand, 0.25–0.1 mm.	Very fine sand, 0.1–0.05 mm.	Coarse silt, 0.05–0.02 mm.	Medium and fine silt, 0.02–0.002 mm.	Clay <0.002 mm.
	(inch)	*pH*	%	%	%	%	%	%	%	%	%
				Paxton fine sandy loam							
A_p	0–8	5.8	3.03	5.2	7.0	6.6	20.4	15.1	19.5	16.1	10.1
B_{21}	8–14	5.9	0.89	5.1	7.4	7.3	22.0	15.8	20.3	16.4	5.7
B_{22}	14–20	6.0	0.42	6.1	8.5	7.7	24.0	16.6	17.8	15.0	4.3
B_3	20–25	6.0	0.22	6.1	8.0	7.8	23.8	16.9	14.8	14.5	8.1
C	25–45	6.2	0.12	5.8	10.0	9.5	27.0	17.4	12.9	11.5	5.9
D_1	45–70	6.4	0.03	5.4	9.4	8.6	25.7	16.7	12.4	13.6	8.2
D_2	70–85	6.2	0.10	5.6	12.3	10.9	27.3	16.6	11.9	10.7	4.7
D_3	85–91	6.4	0.02	5.8	11.0	10.2	27.4	16.3	11.9	10.9	6.5
				Merrimac fine sandy loam							
A_{11}	0–2	3.7	5.34	3.8	12.6	11.6	17.8	12.2	23.6	12.2	6.2
A_{12}	2–3	4.3	2.61	3.4	2.2	21.6	15.9	10.9	26.0	13.3	6.7
A_p	3–8	4.6	0.95	1.5	9.3	10.3	15.5	13.5	29.2	14.3	6.4
B_{22}	8–12	4.5	0.53	2.0	8.8	8.3	11.5	15.3	32.4	14.8	6.9
B_{23}	12–20	4.6	0.26	2.4	10.6	10.6	13.6	17.5	30.8	10.6	3.9
D_1	20–26	4.8	0.08	5.1	21.0	22.0	24.2	8.5	13.2	4.6	1.4
D_2	26–33	4.9	0.07	2.0	6.9	18.9	60.9	7.8	2.3	0.7	0.5
D_3	33–70	4.9	0.02	14.8	28.5	16.3	35.8	2.6	1.1	0.5	0.4

pure described by Bourbeau and Swanson (1). Specific gravity was determined by the standard pycnometer technique.

PHYSICAL ANALYSIS

Table 1 records the mechanical composition of the two soils. The fine sand, very fine sand, and silts are the main components of the Paxton fine sandy loam; for the Merrimac fine sandy loam these sizes are also the main components down to the B_{23} level, but below this horizon coarser particles are more abundant. The texture of the solum of both soils is uniform, a characteristic of brown podzolic soils (12).

The clay contents of both soils are relatively low. The highest clay content in the Paxton is in the A_p (10.1 per cent) followed by the D_1 and B_3 horizons (8.2 and 8.1 per cent, respectively). The Merrimac has uniform clay content from the A_1 to B_{22} horizons (approximately 6.5 per cent), then the clay decreases with further depth.

Data on bulk density and porosity are recorded in table 2. Bulk densities for both soils show gradual increase with depth. Noncapillary porosities decrease

TABLE 2

*Physical properties of Paxton and Merrimac soils**

Horizon	Depth of Sampling	Specific Gravity	Bulk Density	Porosity		
				Capillary	Noncapillary	Total
	inch		*g./cc.*	%	%	%
Paxton fine sandy loam						
A_p	0-2	2.56	0.99	43.3	18.6	61.9
A_p	2-4	2.53	1.04	46.2	22.5	58.7
A_p	5-7	2.56	1.13	39.5	16.3	55.8
B_{21}	8-10	2.60	1.20	37.2	16.6	53.8
B_{21}	11-13	2.60	1.16	35.4	18.7	55.3
B_{22}	14-16	2.57	1.30	37.0	12.3	49.4
B_{22}	17-19	2.61	1.36	35.0	13.4	47.8
B_3	20-22	2.62	1.43	31.5	12.2	45.5
B_3	23-25	2.63	1.59	32.4	7.0	39.4
C	32-34	2.63	1.67	31.2	5.5	36.7
C	38-40	2.62	1.80	30.3	4.5	31.6
C	43-45	2.59	1.82	30.9	1.7	29.7
D_1	49-51	2.58	1.81	30.6	2.7	30.3
Merrimac fine sandy loam						
A_{11}	0.5-2.5	2.49	0.72	59.2	11.9	71.1
A_p	4-6	2.55	1.09	44.6	12.5	57.2
B_{22}	10-12	2.60	1.28	41.9	8.6	50.8
B_{23}	16-18	2.62	1.27	47.8	3.6	51.6
D_1	21-23	2.60	1.40	43.5	2.6	46.1
D_2	26-28	2.60	1.51	31.9	9.8	41.9
D_3	33-35	2.55	1.63	7.6	27.4	35.0

* Average of five determinations. Data, except specific gravity, for Merrimac soils obtained from Bourbeau and Swanson (1).

below the 22-inch level (B_3) for the Paxton; field observations showed that root development was limited to above 25 inches. The high bulk density of the D zone (49–51 inches) is probably due to variation in depth of the compact C horizon at this sampling area. The Merrimac has a very low noncapillary porosity in the 16- to 18- and 21- to 23-inch zones (B_{23} and D_1, respectively).

CHEMICAL ANALYSIS

The elemental composition, heating weight-loss, and "free" iron oxide data for the clay fractions of the two soils are reported in table 3.

The silica content of the Paxton soil clays increases abruptly in the B_3 horizon. The K_2O content, which is used to calculate the illite mineral component, shows a gradual increase with depth. The heating weight-loss data show that the clays are highly hydrated above the B_3 horizon. The B_3, C, and D horizons are relatively constant in total heating weight-loss values.

In the Merrimac, silica is lowest in the B_{22} and B_{23} horizons. Alumina tends to

TABLE 3

Chemical analysis and heating weight-loss data for Paxton and Merrimac soil clays

Size	Horizon	Depth	Oxides*												
			SiO_2	Al_2O_3	Fe_2O_3	TiO_2	K_2O	MgO	200°C. H_2O	300°C H_2O	400°C H_2O	600°C. H_2O	900°C. H_2O	Total	"Free" Fe_2O_3
μ		*inch*	%	%	%	%	%	%	%	%	%	%	%	%	%
Paxton fine sandy loam															
2–0.2	A_p	0–8	34.6	32.1	11.1	0.90	1.96	2.58	5.20	4.77	2.82	3.75	1.12	100.9	—
	B_{21}	8–14	34.6	31.5	11.6	0.98	2.29	2.94	4.12	4.70	3.54	1.55	1.50	99.3	7.5
	B_{22}	14–19	38.9	28.8	9.6	0.73	2.73	3.59	4.58	3.43	3.10	2.47	1.05	99.0	2.8
	B_3	19–24	45.1	27.8	9.6	0.60	3.58	4.30	2.24	1.95	1.56	2.88	1.26	97.2	1.8
	C	24–45	42.0	27.9	10.3	0.42	3.92	4.24	1.56	0.89	2.32	3.54	1.39	98.5	3.2
	D_1	45–70	42.8	27.3	9.3	0.43	4.45	4.08	0.72	0.43	2.80	3.72	1.78	97.8	2.8
	D_2	70–85	41.4	27.6	11.5	0.46	4.41	4.58	2.58	1.64	1.78	3.19	0.94	100.1	—
	D_3	85–91	48.9	25.8	10.4	0.38	4.90	4.16	0.51	0.50	1.26	3.73	1.16	101.7	4.7
<0.2	A_p	0–8	26.8	31.5	13.5	1.52	1.21	1.66	3.54	10.40	3.88	3.37	1.18	98.7	11.2
	B_{21}	8–14	29.7	33.5	13.6	1.63	1.48	1.95	3.17	8.46	3.39	3.26	0.94	101.1	11.7
	B_{22}	14–19	28.6	30.1	11.1	1.38	1.97	2.11	5.79	10.20	4.08	2.87	0.79	99.0	9.0
	B_3	19–25	39.6	28.3	16.2	1.45	1.78	3.76	1.23	3.78	1.96	3.19	0.88	100.7	14.5
	C	25–45	40.0	30.7	13.9	0.90	2.07	2.14	1.18	2.41	2.36	4.83	0.82	101.3	11.9
	D_1	45–70	40.9	27.7	13.7	0.73	2.41	2.22	0.91	1.95	2.06	5.26	0.85	98.7	11.1
	D_2	70–85	37.8	28.1	15.0	1.04	2.53	2.79	2.28	3.49	2.52	3.30	0.83	99.7	11.7
	D_3	85–91	38.7	22.5	21.0	0.86	3.13	2.89	1.85	2.05	1.45	3.62	0.76	98.8	17.6
Merrimac fine sandy loam															
2–0.2	A_{11}	0–2	41.8	24.0	7.4	0.54	1.77	1.40	3.38	13.90	3.38	3.12	1.43	102.1	4.7
	A_{12}	2–3	33.6	31.4	11.7	0.87	1.33	1.37	1.84	11.30	4.56	0.84	1.63	100.4	8.8
	A_p	3–8	34.9	36.3	11.9	0.71	1.52	1.74	1.67	5.82	3.09	1.82	2.38	101.8	9.1
	B_{22}	8–12	31.5	38.0	11.6	0.97	1.46	1.61	1.27	8.30	3.06	2.14	1.32	101.2	7.2
	B_{23}	12–20	32.6	36.8	11.2	1.21	1.78	1.70	2.12	7.62	2.80	2.17	2.07	102.1	6.8
	D_1	20–26	41.1	32.2	8.7	0.45	2.98	2.12	2.53	4.61	2.03	1.74	2.03	100.5	4.7
	D_2	26–33	46.3	30.2	7.3	0.34	3.89	2.98	0.88	3.95	1.56	1.97	1.61	101.0	3.3
	D_3	33–70	49.9	29.2	6.1	0.24	3.89	2.74	0.97	3.20	0.97	2.21	1.78	101.3	2.3
<0.2	A_{11}	0–2	25.8	19.7	12.5	1.26	0.76	1.02	11.0	15.80	6.94	2.89	1.39	99.1	—
	A_{12}	2–3	26.4	25.9	16.9	1.20	0.67	1.12	5.80	11.70	2.45	3.40	1.70	97.2	—
	A_p	3–8	23.1	34.1	17.0	1.13	0.49	0.90	5.36	6.10	4.10	3.52	1.79	97.6	—
	B_{22}	8–12	23.7	34.0	16.4	1.25	0.64	1.04	4.86	9.10	2.63	3.20	1.19	98.0	—
	B_{23}	12–20	21.6	31.9	15.9	1.39	0.72	1.17	5.35	9.96	4.53	3.12	1.94	97.6	—
	D_1	20–26	32.7	27.8	14.9	1.09	1.72	1.87	4.68	4.89	3.60	3.39	2.52	99.2	—
	D_2	26–33	29.7	30.2	12.4	0.34	2.24	2.82	3.18	6.49	3.44	3.58	5.56	100.0	—
	D_3	33–70	35.6	28.7	13.3	0.27	3.01	2.83	1.02	5.16	5.67	2.06	2.58	100.2	—

* Data reported on oven-dry weight basis as averages of duplicate determinations for K_2O and heating weight-loss data.

be high where silica is low. In general, the heating weight-loss is highest near the surface and decreases with depth. The K_2O content increases with depth.

Comparison of the two soils shows that alumina is generally higher in the Merrimac. Comparison of the two clay fractions reveals higher alumina in the coarse fraction of the Merrimac and in the fine fraction of the Paxton. Although "free" iron oxide was not determined for the fine clay fraction of the Merrimac because of the limited amount of sample, it is believed that most of the iron is in the oxide form. Calcium, which is generally present as an exchange cation, was removed by acidification prior to chemical analysis. Tests for its presence by the "Versenate" method proved negative. The Paxton has a higher MgO content than the Merrimac, which is in accord with the parent materials for both soils. The Paxton has a more basic parent material, containing magnesium-bearing minerals such as garnet and biotite; the Merrimac is derived from more acid granitic material.

The total "free" oxide contents of the Paxton and Merrimac soils are recorded in table 4. The analysis employed the method of Jeffries (7) on the <2-mm. particles. The Paxton has a relatively high "free" alumina content in the B_3

TABLE 4

*Total free oxide content of Paxton and Merrimac soils**

Horizon	Depth	Oxides				Total
		SiO_2	Fe_2O_3	Al_2O_3	MnO	
	inch	%	%	%	%	%
Paxton fine sandy loam						
A_p	0–8	0.65	1.75	2.67	0.04	5.11
B_{21}	8–14	0.75	1.61	2.26	0.02	4.64
B_{22}	14–19	0.85	1.16	1.85	0.01	3.87
B_3	19–25	0.75	1.38	2.40	0.01	4.54
C	25–45	0.49	1.52	1.44	0.02	3.47
D_1	45–70	0.53	1.79	0.74	0.02	3.08
D_2	70–85	0.65	1.17	1.88	0.02	3.72
D_3	85–91	0.43	1.45	1.44	0.02	3.34
Merrimac fine sandy loam						
A_{11}	0–2	0.29	1.43	1.25	0.01	2.98
A_{12}	2–3	0.41	1.47	1.42	0.01	3.31
A_p	3–8	0.42	1.49	1.61	0.01	3.53
B_{22}	8–12	0.67	1.68	1.80	0.01	4.16
B_{23}	12–20	0.35	1.19	1.55	0.01	3.10
D_1	20–26	0.29	0.69	0.91	0.01	1.90
D_2	26–33	0.30	0.78	0.62	0.02	1.72
D_3	33–70	0.41	0.50	0.50	0.02	1.43

* Average of duplicate 2.0-g. samples of <2 mm. soil. Data for Merrimac soils obtained from Bourbeau and Swanson (1). Phosphorus, which was removed by the treatment, was not determined.

TABLE 5

Mineralogical content of the clay fractions of Paxton and Merrimac soils*

Size	Horizon	Depth	Qr	Fl	Chl	Ill	Interst. Ill-Verm	Verm	Mont	Kl	Gb	Hm	Total
μ		*inch*	%	%	%	%	%	%	%	%	%	%	%
						Paxton fine sandy loam							
2–0.2	A_p	0–8	<5	<5	<5	30	—	30	0	10	5	5	<95
	B_{21}	8–14	<5	<5	<5	25	15	20	0	10	5	5	<100
	B_{22}	14–19	<5	<5	<5	30	20	15	0	10	0	3	<93
	B_3	19–25	<5	—	<5	30	35	10	0	10	0	2	<97
	C	25–45	<5	—	<5	30	45	5	0	10	0	3	<103
	D_1	45–70	<5	—	—	40	45	0	0	10	0	3	<103
	D_2	70–85	<5	—	—	40	45	0	0	<10	0	—	<100
	D_3	85–91	<5	<5	—	45	45	0	0	5	0	5	<110
<0.2	A_p	0–8	0	0	0	20	—	45	0	—	10	10	85
	B_{21}	8–14	0	0	0	25	—	45	0	—	<10	10	<90
	B_{22}	14–19	0	0	0	20	15	40	0	—	5	10	<90
	B_3	19–25	0	0	0	20	45	10	0	—	0	15	<90
	C	25–45	0	0	0	15	50	5	0	—	0	10	<80
	D_1	45–70	0	0	0	15	60	0	0	—	0	10	85
	D_2	70–85	0	0	0	20	60	0	0	—	0	10	90
	D_3	85–91	0	0	0	25	50	0	0	—	0	15	90
						Merrimac fine sandy loam							
2–0.2	A_{11}	0–2	5	<5	0	25	0	30	15	<10	5	5	<100
	A_{12}	2–3	0	<5	<5	20	0	35	—	15	10	10	<100
	A_p	3–8	<5	<5	<5	25	0	25	—	15	10	10	<100
	B_{22}	8–12	<5	<5	<5	20	0	25	—	15	15	5	<95
	B_{23}	12–20	<5	10	5	25	0	20	—	15	10	5	<95
	D_1	20–26	5	10	5	45	0	10	—	15	5	5	100
	D_2	26–33	5	10	5	60	0	5	—	10	5	3	103
	D_3	33–70	5	10	5	60	0	0	—	10	5	2	97
<0.2	A_{11}	0–2	0	0	0	10	0	10	55	—	5	10	90
	A_{12}	2–3	0	0	0	10	0	10	50	<5	10	15	<100
	A_p	3–8	0	0	0	5	0	40	10	<5	15	15	<90
	B_{22}	8–12	0	0	0	10	0	35	<5	<5	20	15	<90
	B_{23}	12–20	0	0	0	10	0	35	—	<5	15	15	<80
	D_1	20–26	0	0	0	25	0	35	—	5	10	10	<85
	D_2	26–33	0	0	<5	35	0	35	—	5	10	5	<95
	D_3	33–70	0	0	5	45	0	20	—	5	10	5	<90

* Qr = quartz; Fl = feldspars; Chl = chlorite; Ill = illite; Interst. = interstratified; Verm = vermiculite; Mont = montmorins; Kl = kaolin; Gb = gibbsite; Hm = hematite. Zero (0) indicates tests showed absence of mineral in question; dash (—) indicates presence of mineral is doubtful.

horizon. This horizon also contains a high amount of clay (table 1). The highest free alumina in the Merrimac is in the B_{22} horizon, which also contains the highest gibbsite content (table 5). "Free" iron and silica are higher in the Paxton; both soils have very low "free" manganese contents.

MINERALOGICAL COMPOSITION

The coarser fractions of the silts and sands of both soils contained high amounts of quartz and feldspars. Micas were more abundant in the silt than in the sand fractions. Approximate amounts of each major constituent based solely on x-ray diffraction intensities are 50, 30, and 20 per cent, respectively, for quartz, feldspars, and micas.

The clay mineral distribution for the two soils is shown in table 5. In the Paxton profile the clay mineral changes are most noticeable at the 19-inch level (B_{22}); this abrupt change was also noticed in the heating weight-loss data (table 3). Above 19 inches the clay minerals are characterized by increased hydration. Vermiculite increases in abundance with proximity to the surface. The vermiculite reported for these two soils resembles the description of dioctahedral vermiculite reported by Brown (3). Below 19 inches the mineral of greatest abundance is a randomly interstratified vermiculite-illite. The x-ray diffraction patterns for the >19-inch depth were characterized by a maximum at 11.5 A. with no evidence of a peak at 22 A. The 11.5 A. spacing is due to the presence of a randomly interstratified system of 14 A. and 10 A. components. Heating the clays to 400°C. collapsed the mineral to give only a 10 A. spacing; the interpretation for this behavior is that the 14 A. component is vermiculite. The position of the 003/004 spacings in the vicinity of 3.4 and 3.6 A. was used to calculate the fraction of hydrated component. The curves of Brown and MacEwan (2) were consulted for this determination.

The final clay mineral percentages were derived from x-ray, differential thermal, elemental composition, heating weight-loss, and exchange-capacity data. Although the mechanical analyses recorded in table 1 make no differentiation of the clay fraction, the two subdivisions of the clay sizes were made by centrifugation. The coarse clay fraction comprised more than 70 per cent of the total clay.

In the Paxton profile the illite content of the fine clay is lower than that of the coarse clay. The interstratified illite-vermiculite and vermiculite, however, are more abundant in the fine clay fraction. The hematite content based on the 2.70 A. line is relatively high in the fine clay fraction. The outstanding feature of the Paxton clay is the presence in the D horizons of a strong diffraction peak at 11.5 A., which increases in spacing and decreases in intensity with proximity to the surface.

In the Merrimac profile the outstanding feature is the concentration of gibbsite in the B_{22} horizon. The A horizon of the Merrimac is characterized by the presence of montmorin; the montmorin contest is much higher in the fine clay fraction. The identification of montmorin is related to the decrease in alumina (table 3). Whereas vermiculite is the end product of weathering in the Paxton

soil, montmorin is the resultant mineral in the Merrimac soil. The Merrimac has slightly more quartz and feldspars in the lower horizons than has the Paxton. The chlorite content of the Merrimac soil decreases with proximity to the surface; this is in contrast to the higher chlorite content in the upper part of the Paxton soil, though the difference is only slight. Nonoriented-powder camera patterns revealed absence of biotite-type mica in the Merrimac and a relatively high content of this type in the Paxton. The latter, if present as biotite, can weather to chlorites.

DISCUSSION

Paxton fine sandy loam is similar in several respects to Wethersfield silt loam previously reported (13). Both soils are characterized by a compact layer about 20 inches below the surface. The highly weathered surface horizons of both soils contain vermiculite and illite in large quantities. The clays of the C and D horizons differ by the presence of interstratified illite-vermiculite in the Paxton and interstratified chlorite-montmorin in the Wethersfield. The difference can be attributed to differences in parent material; the Wethersfield is developed on till derived from Triassic sandstone, siltstone, and shale that has calcareous lenses or may be faintly calcareous. Montmorins and chlorites are commonly associated with calcareous conditions. Vermiculites and illites are closely associated with biotite, which is abundant in the Paxton. Both soils show rather abrupt increases of vermiculite in the horizons immediately above the compact horizon. The total free oxides also show an abrupt increase in this horizon, "free alumina" being relatively high (table 4) in the Paxton. This leads to a consideration of fragipan. Some of the properties exhibited by the Wethersfield and the Paxton which are associated with fragipans are the compact nature of the horizon or horizons which soften when wet, the acid pH, "free alumina" content,[4] and increases of very fine sand, silt, and clay. The nature of fragipan formation is not definitely known, but certain relationships appear to exist among the properties mentioned.

The clay mineral studies reveal the importance of an acid condition for the formation of brown podzolic soils and fragipans. The acid condition has produced "hydrogen"-saturated clays, although the mineral is highly saturated with alumina and iron oxides in interlayer positions. In clays, hydrogen saturation results in a hydrogen-aluminum-saturated system. Since the aluminum originates from the clay lattice, the clay would be rendered relatively unstable. Thus this situation may be the cause of the low clay content of brown podzolic soils and certainly plays an important role in clay mineral genesis. The presence of aluminum occupying interlayer spaces of clays was shown by Brown (3); and since the clays reacted similarly to the tests conducted by Brown, it is likely that the vermiculite identified in this study is saturated with aluminum to a high degree. The nature of the alumina on the clays would explain the negative gibbsite tests observed with differential thermal analysis. Thus acid

[4] From personal communications with G D. Smith, Soil Conservation Service, Washington, D. C.

pH and "free alumina" are closely related. The higher clay content of the Paxton fragipan horizon may be attributed to the higher pH (pH 6.0) in contrast to the lower clay content of the Wethersfield fragipan (pH 4.6), which has undergone intensive acid leaching and consequent decomposition (13).

Carlisle[5] reasons that the basal till of soils developing fragipans was originally compact and was subjected to processes of freezing and thawing, wetting and drying, biological activity, and weathering to decrease their compaction; but pedological process of deposition of material in the pores and cracks maintained their high bulk density and low permeability. If both geologic and pedologic factors cause fragipan formation, it seems desirable to study the formation (if any of fragipans in soils that have not undergone previous geologic compression. The Merrimac soil of this study appears to show the formation of fragipan without the geologic factor of compression involved.

The wooded Merrimac profile shows several characteristics commonly associated with fragipans. The pH is low (pH 3.7 to 4.9); cation saturation of the B and D horizons is low (4.2 and 2.8 per cent in the B_{22} and B_{23}); and "free alumina" is high in the B horizons. Although the "free" alumina is reported as gibbsite, tests showed that part of the "free" alumina is associated with vermiculite.

Field observations of the Merrimac do not reveal a compact layer in the B horizon similar to that of the Wethersfield or Paxton. The profile description, however, notes that the B_{23} horizon is massive in places but crushes into soft crumbs. In view of this, it may be suitable to quote Winters and Simonson (14): "Furthermore, they [fragipans] exist in all degrees of development from faint ones which are barely evident under favorable moisture conditions to prominent ones which seem completely indurated when dry." Bourbeau and Swanson (1) have reported that the permeability of the 16–18-inch zone is 1.2 inches per hour as compared to 8.1 inches per hour in the 4–6-inch zone. Furthermore their data show that the noncapillary porosity is as low as 3.6 per cent in the 16–18-inch zone. In this soil there is evidence of a weak or incipient fragipan.

Studies by Bourbeau and Swanson (1) have shown that the heavy-mineral distribution for the Merrimac is correlated with rate of flow; the D horizon contained the highest amount, followed by the B and A horizons. If this is so, then one would expect to find the coarser particles highest in the D horizons and the finer silt sediments increasing with proximity to the surface. The mechanical analysis (table 1) reveals that the particle size distribution is marked by a rise in very fine sand and coarse silt in the B_{22} and B_{23} horizons. This type of distribution pattern is in line with Carlisle's theory on the mode of fragipan formation. Another possible explanation is eolian deposition of sediments during glacial time.

One of the ways the Merrimac profile differs from the Paxton is in the presence of montmorin in the A horizons (table 5). The decrease in alumina content in the surface of the Merrimac soil (table 3) is probably closely related to the

[5] Carlisle, F. J. Jr. Characteristics of soils with fragipan in a podzol region. 1954. (Unpublished Ph.D. thesis. Copy on file Cornell University Library, Ithaca, N. Y.)

occurrence of montmorin. It is highly probable that the nonremoval or slow removal of alumina in the Paxton clays has prevented the formation of montmorins. On the other hand, leaching is relatively strong in the Merrimac, as evidenced by the low pH (pH 3.7), and caused the removal of alumina from the clay plates, thus allowing the weathering to proceed to the montmorin stage. This strong acid leaching has caused discontinuous gray A_2 layers to form and probably explains why brown podzolic soils occasionally have a thin A_2 in contrast to the thick A_2 of podzols.

The presence of alumina as gibbsite and "free" iron in the Merrimac soil may help to explain the suitability of this soil for tobacco, a crop commonly associated with more tropical conditions than exist in southern New England today. Tropical soils are generally high in gibbsite and free iron oxides.

The formation of alumina as gibbsite, as interlayer sorbed alumina, and perhaps as amorphous alumina, has important bearing on crop production. Aluminum toxicity has been reported by Hawkins *et al.* on potatoes grown in Connecticut (6). Struchtemeyer *et al.* (11) reported that elimination of phosphorus from fertilizer treatments in Maine reduced potato yields significantly even when the soil contained high amounts of total phosphorus. Tobacco fertilization with phosphate is aimed at reducing aluminum uptake as well as supplying sufficient phosphate to the plant. Aluminum in high amounts imparts poor quality to tobacco leaves.

The results of this study have shown that the clays are high in free alumina and iron. Since both plant roots and clays are involved in exchange reactions, it is very important to consider the alumina and iron in these clays. The growing of tobacco and potatoes in acid media makes it even more important to consider the genesis of brown podzolic soils. Further studies on their genesis should make possible better utilization of the phosphorus in soils and fertilizers.

SUMMARY

The mechanical analysis of two soils from Connecticut showed relatively low clay content (approximately 5 per cent). The particle size distribution of the profiles was related to the presence of fragipan. The elemental composition was marked by increases in silica, potassium, and magnesium with depth; alumina decreased with depth in the Paxton soil but reached a maximum in the B_{22} horizon in the Merrimac soil.

The mineralogical determination of the Paxton soil showed illite and vermiculite to be the chief components in the <19-inch depth (approximately 20 per cent each); interstratified illite-vermiculite was most abundant below 19 inches (approximately 50 per cent). Small quantities of gibbsite (5 per cent) were identified above 19 inches.

The Merrimac soil showed maximum gibbsite in the B_{22} horizon (approximately 15 per cent), which is in accord with chemical analysis. Montmorin was present in the A horizon of the Merrimac.

Both soils contained vermiculite, which was high in aluminum saturation; it is possible that the aluminous condition of these soils is responsible for much of the phosphate deficiency and aluminum toxicity found in crops grown in them.

It is also probable that the low clay content encountered in brown podzolic soils is caused by the dealumination reaction, which would foster clay decomposition.

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CALCIUM-BORON RELATIONSHIPS IN SIBERIAN MILLET

WAYNE J. McILRATH AND JAN A. DEBRUYN

University of Chicago[1]

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There have been numerous reports (15) of the occurrence of symptoms of boron deficiency in plants on overlimed soils, even when the soils, themselves, contained appreciable quantities of boron. Though many investigations, in which controlled nutrient levels were used, have also indicated a calcium-boron relationship in the absorption and metabolism of these elements by plants (2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 13, 16, 17, 19), the majority concern dicotyledonous plants only. Among the monocots only corn and oats apparently have been studied. To obtain additional information concerning the effects of various calcium and boron treatments on the growth and chemical composition of another monocot, Siberian millet, was the purpose of the investigation reported here.

MATERIAL AND METHODS

Cultural methods

Plants were grown in purified quartz sand in the greenhouse at Chicago, Illinois. Impurities were removed from the sand by a 10-hour leaching with 10 per cent HCl followed by thorough washings with tap water, distilled water, and finally demineralized water. Uniform quantities of sand were placed in each of five half-gallon glazed pots randomly distributed on the bench. On April 8 seeds of Siberian millet, *Setaria italica* Beauv., were planted directly in the sand. The resulting seedlings were thinned to a uniform stand of four per pot. To exhaust residual nutrients in the seeds and sand, seedlings were supplied with demineralized water for 10 days subsequent to planting, and with half-strength nutrient solutions (minus boron) for an additional 10 days. Thereafter, the full nutrient treatment was continued for 35 days. The plants were flowering at the time of harvest on June 2.

The composition of the nutrient solutions at four calcium levels, with five boron concentrations in each calcium series is given in table 1; the pH of each solution was adjusted to the value indicated. Reagent grade chemicals and demineralized water were used in the preparation of the solutions, which were stored in soft-glass carboys. Uniform amounts of nutrient solution were applied every third day and demineralized water containing 5 mg. iron tartrate per liter on the day preceding nutrient application.

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TABLE 1

Composition of nutrient solutions at four different calcium levels

Calcium Levels	Millimolar Concentrations of Major Salts†						pH
	KNO_3	$Ca(NO_3)_2$	$MgSO_4$	$(NH_4)_2HPO_4$	$CaCl_2$	$NaNO_3$	
*ppm.**							
40	6.0	1.0	2.0	1.0	—	6.0	6.2
160	6.0	4.0	2.0	1.0	—	—	6.1
320	6.0	4.0	2.0	1.0	4.0	—	6.1
480	6.0	4.0	2.0	1.0	8.0	—	6.0

* Each calcium level supplied with boron (as H_3BO_3) in concentrations of 0.00, 0.05, 0.50, 5.0, and 50.0 ppm. B.

† Micronutrients added to all nutrient solutions in the following concentrations: manganese, as $MnCl_2 \cdot 4H_2O$: 0.5 ppm. Mn; copper, as $CuSO_4 \cdot 5H_2O$: 0.02 ppm. Cu; zinc, as $ZnSO_4 \cdot 7H_2O$: 0.05 ppm. Zn; molybdenum, as $H_2MoO_4 \cdot H_2O$: 0.01 ppm. Mo.

Analytical methods

The tops of two of the four plants in each pot were frozen immediately after being harvested and were subsequently used for determination of soluble calcium. The tops of the other two plants in each pot were dried, ground (60-mesh), and analyzed for total calcium, total boron, and residual boron. Tops and roots were dried in a forced-draft oven for 48 hours at 80°C. to obtain their dry weights.

The frozen fresh material was extracted with demineralized water in a Waring blendor for 5 minutes, after which the extracts were decolorized with activated carbon, filtered, and analyzed for soluble calcium. Because of impurities in the carbon and interference by nitrates and organic materials these extracts could not be used for determination of soluble boron.

Residual boron was determined after aqueous extraction of the dried tissue for 30 minutes in a water bath at 80°C. After three hot-water washings by centrifugation the residue was quantitatively transferred to a filter paper, dried, ashed at 450°C., and analyzed for residual boron.

After the dry material was ashed at 450°C., the ash was dissolved in 0.36 *N* H_2SO_4 and filtered. The filtrate was then analyzed for total calcium and total boron. Calcium was determined turbidometrically (20), and boron by the quinalizarin method (1), with a Klett-Summerson photoelectric colorimeter. Soluble boron was calculated as the difference between total and residual boron (4, 6, 16). Results were analyzed statistically, according to established methods (18).

RESULTS AND DISCUSSION

Plant Growth

Regardless of calcium treatment (table 2), with few exceptions boron applications between 0 and 0.5 ppm. had no significant effect on the dry weight of tops and roots. At the intermediate calcium levels (160, 320 ppm.) 5.0 ppm. boron caused a significant decrease in dry weights; 50 ppm. resulted in a highly significant decrease.

The percentage dry weight of tops was found to be lowest in plants receiving 50 ppm. boron (table 2). This response of millet to high boron concentrations appears to be at variance with that reported for soybean by Minarik and Shive (13), who found that high levels of boron tended to reduce the plant water content. In the present study boron concentrations between 0 and 0.5 ppm. did not have a significant effect on the percentage dry weight. With the lowest boron concentration, increased calcium supply had no significant effect on percentage dry weight; at higher boron levels, the percentage dry weight showed a tendency to increase with the calcium supply. Significant differences occurred mostly between 40 and the 320 or 480 ppm. calcium levels. Analysis of variance indicated, however, that both boron and calcium supply affected the percentage dry weight of the tops, and thus the plants, in a highly significant manner.

Calcium generally had no significant effect on the dry weight of roots. In terms of dry weight, the roots of plants receiving 160 ppm. calcium and 0.5 ppm. boron exhibited the best growth. At 0 and 0.05 ppm. boron, highest yields of tops were obtained with plants receiving 320 ppm. calcium; at 0.5 ppm. boron

TABLE 2

Effects of different calcium and boron treatments on dry weight of tops and roots, top-root ratio, percentage dry weight, and percentage ash of tops of Siberian millet

Treatment		Dry Weight		Top-Root Ratio	Tops	
Ca	B	Tops	Roots		percentage dry weight	percentage ash
ppm.	*ppm.*	*g.*	*g.*			
40	0.00	1.53	0.29	5.42	16.32	12.06
40	0.05	1.55	0.26	5.96	16.90	11.34
40	0.50	1.55	0.27	5.77	16.02	12.65
40	5.0	1.31	0.22	5.91	15.37	14.69
40	50.0	0.34	0.06	5.70	13.09	18.50
160	0.00	1.71	0.26	6.60	17.66	10.15
160	0.05	1.51	0.30	5.07	16.63	11.39
160	0.50	1.97	0.36	5.58	19.45	10.36
160	5.0	1.39	0.22	6.33	16.75	12.56
160	50.0	0.40	0.06	6.06	13.90	15.21
320	0.00	1.81	0.27	6.73	18.63	9.41
320	0.05	1.89	0.28	6.80	18.72	9.47
320	0.50	1.86	0.31	5.95	18.88	9.51
320	5.0	1.41	0.22	6.55	16.55	10.46
320	50.0	0.53	0.08	6.66	14.90	14.10
480	0.00	1.63	0.24	6.79	17.87	9.84
480	0.05	1.77	0.26	6.73	18.38	10.41
480	0.50	1.58	0.23	6.84	17.07	10.88
480	5.0	1.63	0.25	6.45	17.81	11.16
480	50.0	0.54	0.08	6.33	16.08	12.84
L.S.D.	(0.05)	0.28	0.056	0.98	1.81	1.24
L.S.D.	(0.01)	0.37	0.075	1.30	2.40	1.65

with 160 ppm. calcium; and at 5.0 and 50.0 ppm. boron with 480 ppm. calcium. Although the dry weight of tops increased with the calcium supply at higher boron levels, the only significant difference was observed between 40 and 480 ppm. calcium, at 5.0 ppm. boron (table 2). Other investigators (2, 16) have suggested that the toxic effects of boron may be alleviated by increased calcium supply.

Analysis of variance showed that boron supply had a highly significant effect on the dry weights of tops and roots; calcium affected only the tops to such a degree. A significant interaction between the effects of calcium and boron on root weight was also indicated. With the concentrations employed, boron affected the dry weights of tops and roots to a greater degree than did calcium, even though the range in boron concentrations was smaller than that of calcium (table 2).

The top-root ratio generally was not significantly affected by the boron supply (table 2). Only at the lower boron concentrations did calcium have any significant effect upon this ratio. In general, increased calcium supply tended to effect an increase in the ratio, and analysis of variance showed calcium to influence the ratio in a highly significant manner.

Deficiency and toxicity symptoms

After application of full-strength nutrient solution for 2 weeks, visual calcium-deficiency symptoms began to appear in all plants receiving 40 ppm. calcium with the exception of those supplied with 50 ppm. boron. The tips of younger leaves became chlorotic and shriveled or curled; necrosis followed in some plants. No definite calcium-toxicity symptoms were recognized during the experiment.

At no time during the experiment were any definite symptoms of boron deficiency observed in any treatment. It has been reported (6) that in comparison with long-day conditions of summer, under short-day conditions of spring and autumn the onset of boron deficiency is delayed. Since the present experiment was conducted during the spring months, this factor may have contributed to the absence of boron-deficiency symptoms. On the other hand, the boron content of plants in this study, even on the 0.0 ppm. boron level, was generally higher than that found by Hernandez-Medina (6) in corn plants exhibiting deficiency symptoms.

Boron-toxicity symptoms became visible in all plants supplied with 5.0 and 50.0 ppm. boron after 1 week of full-nutrient application. In these series the initial manifestation was a "burning" of the leaf tips, which was followed later by development of necrotic spots along the margins of the leaves. Boron-toxicity symptoms were most marked in plants of the 50.0 ppm. series, in which the degree of necrosis progressed with age and the lower leaves eventually died.

Chlorosis resulting from boron toxicity seemed to decrease as the plants increased in size; and boron-toxicity symptoms were apparently reduced as the calcium supply was increased. Although the reduction of boron-toxicity symptoms was not sufficient to warrant definite conclusions, calcium may have

counteracted the toxic effects of boron to some extent, as has been similarly observed by several workers (4, 6, 12, 16).

Composition of tops

Increase in the boron supply from 0 to 50.0 ppm. at all calcium levels resulted in a highly significant increase in the ash content of the millet plants (table 2). In soybeans, however, Minarik and Shive (13), found no such effect of increased boron supply. In contrast to boron, increased calcium levels generally resulted in a decrease in the percentage ash. This was increasingly evident at the higher boron levels. Analysis of variance indicated that both boron and calcium had a highly significant effect on the percentage ash.

Since the seeds used in this investigation contained only 0.003 ± 0.001 mg. boron per gram (about 0.007 μg. per seed), the boron content of the plants of the 0 ppm. series cannot be accounted for from this source. Obviously, therefore, these cultures, in spite of the precautions taken, had a slight contamination of boron, but this amount appears to have been enough to prevent the appearance of visual deficiency symptoms in this series. Why plants of the 0 ppm. boron series contained more boron than did those of the 0.05 ppm. group is not known.

Although increased boron applications up to 0.5 ppm. resulted in no significant increase in soluble and total boron contents of the tops, 50 ppm. resulted in a highly significant increase, regardless of calcium treatment (table 3). Boron application of 5.0 ppm. resulted in a significant increase of soluble and total boron compared to the lower boron levels in the 40 and 160 ppm. calcium series, but at a calcium level of 320 ppm., the plant boron content could only be said to have increased significantly when the increase is compared to applications of 0.05 ppm. and below. In the 480 ppm. calcium series, 5.0 ppm. boron did not result in a significant increase in these fractions over the lower levels of application. Analysis of variance indicated boron supply to have a highly significant effect upon total and soluble boron content.

Even though increased substrate calcium generally resulted in a lower total boron content of the plants (4, 5, 16), it was only at the highest boron level that such an increase resulted in a significant decrease in both total and soluble boron. With increased calcium supply, however, the percentage of soluble boron tended to increase. Millet, like other monocots investigated (6, 10, 11, 17), maintained a major portion of its boron in soluble form.

At a given calcium level, boron solubility, with one exception, decreased with increased boron supply from 0 to 0.05 ppm. and then increased with boron applications of 0.5 ppm. and above. At boron supplies between 0 and 0.5 ppm. the effect of calcium on boron solubility was inconsistent. Boron supplies of 5.0 and 50.0 ppm. generally resulted in a slight increase in the percentage of boron in the plant in soluble form (6, 11).

Generally, the boron supply did not significantly affect the total calcium content except at the highest calcium level, where a significant difference did occur but with too little consistency to indicate a trend. In only one instance was the soluble calcium content significantly affected by either boron or calcium

TABLE 3

Total and soluble boron and calcium content of Siberian millet, as affected by different calcium and boron treatments

Treatment		Per Gram Dry Weight of Top				Boron: Soluble/Total	Calcium: Soluble/Total	Ratio: Total Ca/Total B
		Boron		Calcium				
Calcium	Boron	Total	Soluble	Total	Soluble			
ppm.	*ppm.*	*mg.*	*mg.*	*mg.*	*mg.*	%	%	
40	0.00	0.029	0.022	2.61	0.058	75.9	2.22	90.0
40	0.05	0.020	0.009	2.41	0.093	45.0	3.86	120.5
40	0.50	0.043	0.026	2.74	0.260	60.5	9.49	63.7
40	5.0	0.262	0.231	3.79	0.260	88.2	6.86	14.5
40	50.0	1.166	1.100	4.16	1.165	94.3	28.00	3.6
160	0.00	0.040	0.030	5.08	0.126	75.0	2.48	127.0
160	0.05	0.026	0.011	6.25	0.146	42.3	2.34	240.4
160	0.50	0.045	0.030	5.40	0.135	66.7	2.50	120.0
160	5.0	0.278	0.249	6.68	0.188	89.6	2.81	24.0
160	50.0	0.879	0.814	9.03	4.639	92.6	51.37	10.3
320	0.00	0.017	0.001	6.67	0.152	5.88	2.28	392.4
320	0.05	0.016	0.001	6.78	0.079	6.25	1.17	423.8
320	0.50	0.037	0.018	7.88	0.261	48.6	3.31	213.0
320	5.0	0.231	0.211	7.46	0.164	91.3	2.20	32.3
320	50.0	0.786	0.776	6.45	0.766	98.7	11.88	8.2
480	0.00	0.014	0.010	5.86	0.085	71.4	1.45	418.6
480	0.05	0.018	0.012	9.08	0.142	66.7	1.56	504.4
480	0.50	0.034	0.028	7.99	0.091	82.4	1.14	235.0
480	5.0	0.194	0.188	10.95	0.265	96.9	2.42	56.4
480	50.0	0.760	0.756	7.50	0.416	99.5	5.55	9.9
L.S.D.	(0.05)	0.203	0.200	1.76	1.662	—	—	—
L.S.D.	(0.01)	0.269	0.265	2.33	2.204	—	—	—

treatment, and that occurred in plants supplied with 160 ppm. calcium and 50 ppm. boron. In this case, regardless of boron or calcium supply, the soluble calcium content was significantly higher than in any other treatment. Analysis of variance, however, indicated boron supply as having a highly significant effect upon both soluble and total calcium content. This seeming discrepancy might be explained by the great variation observed in both total and soluble calcium of different replicates, a factor which probably affected calculation of the least significant difference (table 3). If a correlation, in this study, as indicated in the analysis of variance, truly exists, it appears to be a finding that is opposed to the findings of numerous other studies in which the calcium content of the plants was determined primarily by the calcium content of the substrate and was largely independent of substrate boron concentration (4, 6, 10, 14, 16, 19).

In general, an increased calcium supply was reflected in an increase in total calcium content, regardless of boron treatment. According to analysis of variance,

calcium supply had a highly significant effect upon total calcium content. The interaction between the effects of calcium and boron on total calcium was highly significant; it also affected the soluble calcium content significantly. At a particular calcium substrate concentration, the relative amount of soluble calcium in the plant appeared to be directly related to boron supply. Thus it would appear that at a given level of calcium supply the soluble plant calcium was not so much a function of calcium supply as it was of the boron content of the plant (6, 8, 9, 10, 17). In the higher calcium and boron concentrations, the percentage of soluble calcium decreased with an increase in the calcium supply.

Calcium-boron ratios

As might be expected, plants receiving the lowest levels of substrate boron in each calcium series had the highest Ca/B ratios, and those on the highest levels of boron exhibited the lowest ratios (table 3). Within limits, this quantitative relationship between calcium and boron in the tissues appeared to influence the metabolic activities of the plants. As others have pointed out (7, 11), however, it is doubtful that Ca/B ratios per se are of much value, for they give little indication whether sufficient calcium or boron is present for normal growth. In this study, for example, plants grown on a substrate concentration of 40 ppm. calcium and 0.05 ppm. boron exhibited essentially the same Ca/B ratio as did those on 160 ppm. calcium and 0.50 ppm. boron, yet plants of the former group exhibited definite visual calcium-deficiency symptoms, whereas those of the latter did not. The former series also produced significantly less top growth than did the latter. When calcium was present in the substrate in adequate supply,

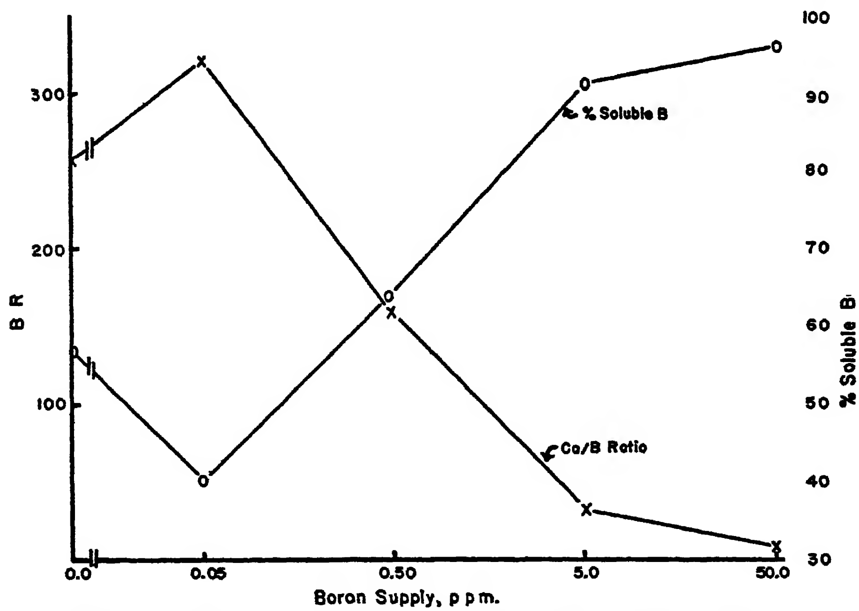

FIG. 1. EFFECT OF BORON SUPPLY ON Ca/B RATIO AND PERCENTAGE OF SOLUBLE BORON

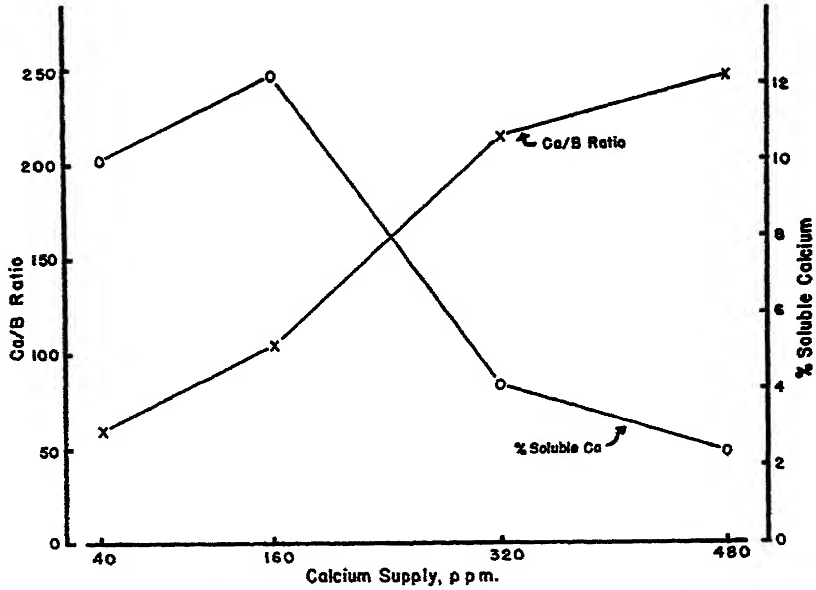

FIG. 2. EFFECT OF CALCIUM SUPPLY ON Ca/B RATIO AND PERCENTAGE OF SOLUBLE CALCIUM

Ca/B ratios between 120 and 500 apparently made little difference in the efficiency of plant growth. Plants showing boron-toxicity symptoms had Ca/B ratios of 56 or less.

In this study an interesting relationship was found between the Ca/B ratio and boron solubility, as affected by boron supply (fig. 1). It was observed that a closer relationship seemed to exist between the Ca/B ratio and boron solubility than between boron supply and boron solubility. Whereas the effect of boron supply was more or less direct, there was an inverse relationship between the Ca/B ratio and percentage of soluble boron. To some degree, the solubility of calcium in the plant, as affected by calcium supply, was also an inverse function of the Ca/B ratio (fig. 2). Generally, the Ca/B ratio increased with calcium supply, whereas the solubility decreased. An exception was noted between 40 and 160 ppm. calcium, where calcium solubility paralleled the Ca/B ratio. Whether this is a normal condition or is caused by the very high solubility of the calcium at 160 ppm. is not known.

SUMMARY

An investigation was carried out on the effects of four different calcium concentrations (40, 160, 320, and 480 ppm.), each supplied with 0, 0.05, 0.5, 5.0, and 50 ppm. boron, on the growth and chemical composition of Siberian millet, *Setaria italica* Beauv. Visual boron-toxicity symptoms developed in all plants receiving 5.0 and 50 ppm. boron; calcium-deficiency symptoms were observed in plants supplied with 40 ppm. calcium. No definite symptoms of either boron deficiency or calcium toxicity were observed.

High boron applications (5.0 and 50 ppm.) generally resulted in decreased dry weight of tops and roots; boron affected the top-root ratio only in isolated cases. Increased boron supply especially at higher boron levels, generally resulted in a decrease in the percentage dry weight and in increased percentage ash of the tops.

Calcium applications had little or no effect upon dry weight of roots. Increased calcium concentrations resulted in limited increase in dry weight of tops, and of top-root ratio. With increasing calcium supply, percentage dry weight generally increased and percentage ash decreased.

Both soluble and total boron and the percentage of soluble boron increased with the boron supply, especially at higher boron levels. Soluble and total calcium and the percentage of soluble calcium were also increased with an increase in boron concentration.

Increased calcium supply resulted in a decrease of soluble and total boron at high boron levels; soluble and total calcium content were increased with the calcium supply. Calcium solubility was decreased and the percentage of soluble boron was slightly increased with increasing calcium applications.

The Ca/B ratio generally increased with calcium supply and decreased with an increased boron supply. An inverse relationship was found to exist between the Ca/B ratio and solubility of boron, as affected by the boron content of the substrate. Similarly, an inverse relationship was demonstrated between the Ca/B ratio and solubility of calcium, as affected by calcium supply.

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EFFECT OF SOIL pH AND CALCIUM ON UPTAKE OF ZINC BY PLANTS

JOHN I. WEAR

Alabama Polytechnic Institute[1]

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Field tests in Alabama have shown that a ton of lime applied to a soil low in available zinc can reduce the yield of corn 10 or more bushels an acre. Previous work (17) demonstrated that this reduction in yield can be prevented by an application of zinc. The objective of the present work was to determine the cause of the increased zinc requirements when lime was applied, or, in other words, to determine whether this lime-zinc problem was a pH effect, a calcium effect, or a combined pH-Ca effect.

Many years ago there was interest in the zinc-lime relationship in the correction of zinc toxicity of plants growing in zinc-coated containers (11) and in peat soils containing toxic concentrations of soluble zinc (16). Additions of lime have corrected plant toxicity that resulted from the addition of large amounts of zinc compounds to the soils (5, 6, 8). Rogers and Wu (13) showed that zinc content of oats decreased with increased rates of lime and increased with increased rates of zinc. Woltz, Toth, and Bear (18) obtained a decreasing uptake of Zn65 in soybeans with increasing rates of limestone. They concluded that applications of limestone resulted in a more pronounced fixation of zinc in the soil than did applications of phosphate. In an experiment measuring the uptake of adsorbed zinc associated with a wide range of Ca and H as complementary ions, Epstein and Stout (4) showed that the uptake of zinc increased with increasing proportions of complementary H ions and decreasing Ca ions. Alben and Boggs (1) found the zinc content of basic soils generally higher than that of acid soils. Peach (12) concluded that as the pH of the soil is increased with $CaCO_3$ the amount of extractable zinc diminishes, and that virtually all the zinc was fixed at pH 9.0. McGeorge (9) found that sulfur and sulfur-manure mixtures increased the zinc content of seedlings, roots, and tops. When zinc was added to the soil, Gall (5) found that soils which absorbed the highest amount were those which were high in organic matter, calcium, and colloidal content. Jones (6) found that zinc added to the soil was held in a replaceable form, and that it replaced principally calcium. Jones, Gall, and Barnett (7) concluded that when zinc was added in high concentrations, it was found not only in water-soluble and replaceable form but in insoluble form also. Mahoric (10) indicated that this may be a simple reaction of $ZnSO_4 + CaCO_3 \rightarrow ZnCO_3 + CaSO_4$; Shaw *et al.* (15), however, reported that very little difference in utilization was obtained from $ZnSO_4$, $ZnCO_3$, zinc in plant material, or residual zinc. Elgabaly (3) concluded that zinc was fixed by various minerals, and Elgabaly and Jenny

[1] Contribution from the department of agronomy and soils, Agricultural Experiment Station, Alabama Polytechnic Institute, Auburn, Alabama.

(2) stated that zinc clay possesses pronounced anion-exchange properties and has a mosaic surface capable of independent cation and anion exchange.

MATERIALS AND METHODS

The soil selected for this study was a zinc-deficient Norfolk sandy loam with a pH value of 5.6 and a base-exchange capacity of 2.2 me. per 100 g. of soil. Eight pounds of soil was potted in 1-gallon cans with polyethylene liners. All lime, gypsum, sodium carbonate, fertilizer, and minor elements were thoroughly mixed with the soil. The soil was moistened, covered, and allowed to stand in the greenhouse for 3 months before a crop was planted. This allowed time for the lime and other added materials to react before zinc uptake by the plant was measured. All effects were measured at three levels of zinc: 0, 20, and 40 pounds of $ZnSO_4$ per acre. Treatments consisted of four rates of $CaCO_3$: 0, 2000, 4000 and 8000 pounds per acre; four rates of Na_2CO_3: 0, 500, 1000, and 2000 pounds per acre; and four rates of $CaSO_4$: 0, 500, 1000, and 2000 pounds per acre. All treatments were replicated three times. The fertilizer consisted of c. p. salts of $NaNO_3$, KH_2PO_4, and KCl at the rate of 1000 pounds of 8–8–8 per acre. Magnesium and minor elements other than zinc were added in amounts believed to be sufficient. Sorghum was selected as the indicator crop because corn seed may be an important source of zinc (15). At the end of a 35-day growing period, dry weights of the ground portion were obtained and analyzed for zinc and calcium. Each pot of soil was thoroughly mixed and sampled. Extractable zinc, exchangeable calcium, and pH were determined for each individual pot. The procedure for determining extractable zinc of soils and total zinc in plant tissue was based on the dithizone procedure of Shaw and Dean (14). Each analysis reported represents an average of three individual replications in each treatment. All water used in the experiment was redistilled from an all-Pyrex still.

DISCUSSION AND RESULTS

An application of $CaCO_3$ at the rate of 2000 pounds per acre considerably reduced the zinc uptake by sorghum (fig. 1). Increased rates of $CaCO_3$ further reduced zinc uptake, but the reduction was not as great as from the first increment of 2000 pounds. These data are in accord with those of Woltz, Toth, and Bear (18). The 2000-pound rate of $CaCO_3$ increased the pH of this soil from 5.7 to 6.6, the calcium content of the plant from 0.78 to 1.09 per cent, and the exchangeable calcium from 0.37 to 3.2 me. per 100 g.

Increased rates of Na_2CO_3 increased the pH of the soil without increasing the calcium content. As shown in figure 2, the uptake of zinc was reduced as the rates of Na_2CO_3 were increased. The pattern in figure 2 follows very closely that of figure 1.

Increasing rates of $CaSO_4$ from 0 to 2000 pounds increased the acidity of the soil and the zinc uptake by the plant. This was a reversal of the effects obtained with the other two materials. The 2000-pound rate of gypsum increased the acidity from a pH value of 5.6 to 4.8, the plant calcium from 0.78 to 1.01 per cent, and the exchangeable calcium in the soil from 0.37 to 0.68 me. per 100 g. Figure 1

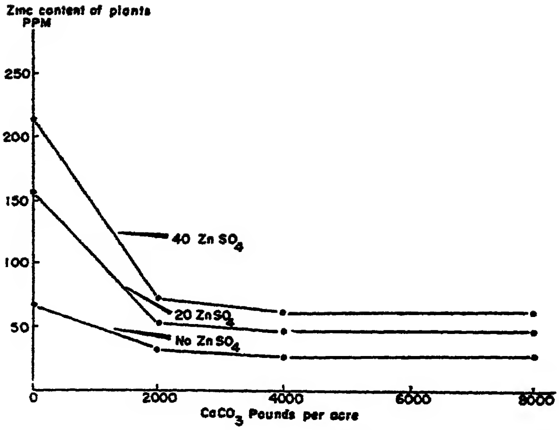

Fig. 1

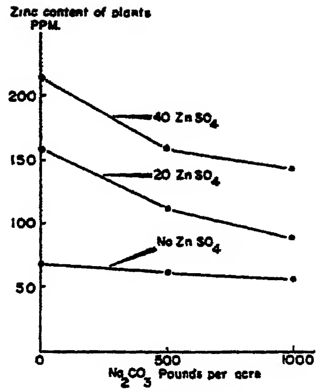

Fig. 2

Fig. 1. Zinc Content of Sorghum from Different Rates of Zinc Sulfate and Calcium Carbonate Added to the Soil in Pounds per Acre

Fig. 2. Zinc Content of Sorghum from Different Rates of Zinc Sulfate and Sodium Carbonate Added to the Soil in Pounds per Acre

indicates that zinc uptake may be affected by pH and calcium or both; figure 2 indicates a pH relationship; and figure 3 indicates that definitely it is not a calcium effect and possibly it is a pH effect.

Figure 4 shows a highly significant relationship between pH value of the soil and amount of zinc taken up by the plant. This figure represents all relationships between zinc uptake and pH values, regardless of whether the pH was obtained from calcium carbonate, sodium carbonate, or calcium sulfate. At each zinc level the effect of pH on zinc uptake was highly significant. As the pH increased, the zinc uptake decreased; the actual amounts of decrease per unit pH change are shown as *b* values. The effect of pH differed highly significantly with

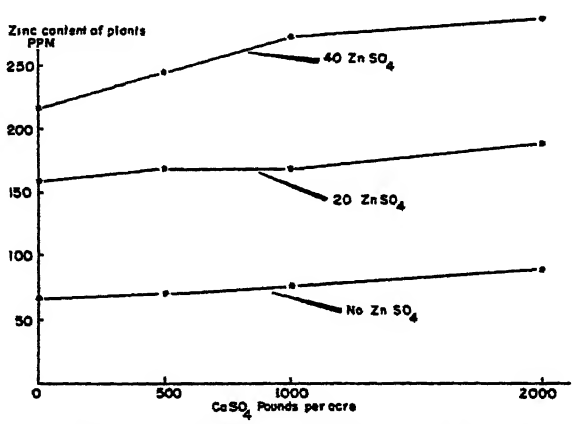

Fig. 3. Zinc Content of Sorghum from Different Rates of Zinc Sulfate and Calcium Sulfate Added to the Soil in Pounds per Acre

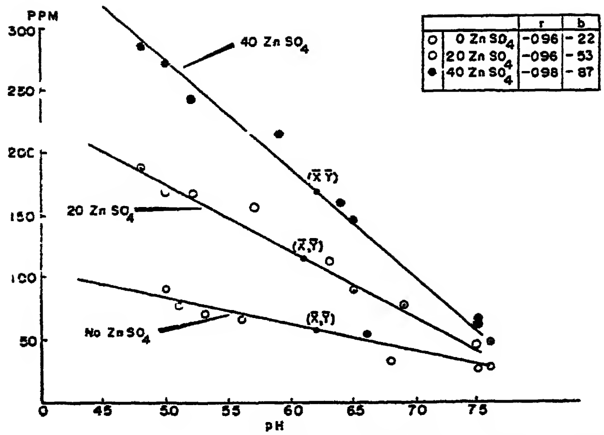

FIG. 4. ZINC CONTENT OF SORGHUM AS AFFECTED BY pH VALUE OF SOIL

The pH values for each level of zinc were obtained from calcium carbonate, sodium carbonate, or calcium sulfate.

the amount of $ZnSO_4$ added to the soil, the effect being greater as more $ZnSO_4$ was added.

It appears likely that a soluble form of zinc at a lower pH may be converted to a less soluble and less available form in the soil at higher pH values. Preliminary data in this study indicate that as the pH of the soil increases, the extractable zinc, as measured by the ammonium acetate-dithizone procedure, decreases. Further work will be done to determine the effect of pH on the availability of zinc in the soil and the less soluble zinc compounds that may be formed.

SUMMARY

$CaCO_3$, $CaSO_4$, and Na_2CO_3 were incorporated in a Norfolk sandy loam at various rates to measure the effects of pH and calcium on the uptake of zinc by an indicator plant in the greenhouse.

An application of 2000 pounds of $CaCO_3$ per acre considerably decreased the zinc content of sorghum. The pH of the soil was increased from 5.7 to 6.6, and the calcium content of the plant was increased from 0.78 to 1.09 per cent. Higher rates of $CaCO_3$ further decreased the zinc content to some degree. Sodium carbonate also reduced the zinc uptake as the pH of the soil increased.

An application of 2000 pounds of $CaSO_4$ per acre did not decrease the zinc content of the plant, but as the pH decreased from 5.6 to 4.8 the zinc content increased slightly and the calcium content of the plant increased from 0.78 to 1.01 per cent.

Graphs showing the effect of pH on the uptake of zinc present conclusive evidence that the reduction in zinc uptake by the plant is a pH effect and not a calcium effect.

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FIXATION AND EXTRACTABILITY OF FISSION PRODUCTS CONTAMINATING VARIOUS SOILS AND CLAYS: I. Sr90, Y91, Ru106, Cs137, AND Ce144

H. NISHITA, B. W. KOWALEWSKY, A. J. STEEN, AND K. H. LARSON

University of California, Los Angeles[1]

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One of the problems which result from atomic detonations and power reactor operations concerns the contamination of soils by fission products. Possible subsequent radiation hazards make such contamination an immediate danger to the soil-plant-animal cycle. The degree of hazard depends upon the quantities of radioactive materials which become available to plants and animals, and the available quantities depend in turn upon the physical and chemical properties of the contaminating material. The purpose of this investigation was to study the relative fixation and extractability of several long-lived and medium-lived fission products from various soils and clay minerals. This was accomplished by leaching contaminated soils and clay minerals with water and various solutions.

MATERIALS AND METHODS

Five radioisotopes (Sr90, Y91, Ru106, Cs137, and Ce144)[2] produced by fission and processed carrier-free were used in these experiments. All were received as cations in the chloride form in HCl solution. Prior to use, Sr89 contaminating the Sr90 solution was allowed to decay. Radioisotopes with radioactive daughters were in secular equilibrium when applied to soils or clays.

Five soils and two clay minerals were selected on the basis of their chemical and physical properties (tables 1 and 2). Mechanical analysis was by the pipette method (3). Except for the extractable Sr levels, the chemical properties were determined by the methods of Peech *et al.* (6). Extractable Sr was determined spectrographically on soil leachate ash samples prepared as follows: 150 g. of soil was leached successively with small aliquots of neutral *N* NH_4Ac until 3 liters of leachate was obtained. The entire volume of the leachate was then evaporated to dryness in a platinum crucible and ashed in a muffle furnace at 520° C. for 12 hours. No detectable amounts of extractable Y, Ru, Cs, and Ce were present in any of the ash samples.

Soil and clay mineral contamination

For leaching experiments, a desired amount of radioisotope solution was measured in duplicate or triplicate into 30-ml. Pyrex beakers and stainless steel

[1] This article is based on work performed under Contract No. AT-04-1-GEN-12 between the Atomic Energy Commission and the University of California at Los Angeles. The authors express appreciation to J. W. Neel and E. M. Romney for their assistance.

[2] Carrier-free radioisotopes were obtained from the Oak Ridge National Laboratory, Oak Ridge, Tennessee

TABLE 1

Chemical properties of soils and clays

Soil or Clay	pH	Organic Matter	Cation-exchange Capacity	Extractable Cations					Predominant Clay Mineral*
				K	Na	Ca	Mg	Sr	
		%	me./100 g.	me./100 g	me./100 g.	me./100 g.	me./100 g.	me./100 g.	
Aiken silty clay loam	5.7	4.15	18.3	0.81	0.14	6.70	0.80	0.004	A
Egbert muck	3.9	32.35	68.2	0.12	0.18	21.20	5.50	0.161	—
Hanford sandy loam	6.6	1.45	8.2	0.37	0.14	4.50	0.26	0.033	B
Sassafras sandy loam	4.6	1.58	6.0	0.01	0.04	0.40	0.02	0.001	A
Vina loam	6.5	0.48	14.3	1.02	0.20	8.20	2.72	0.047	C
Bentonite†	8.2	—	98.3	0.25	1.32	69.00	16.60	0.274	—
Kaolinite†	4.3	—	5.5	0.09	0.57	3.60	0.52	0.006	—

* A, kaolinite; B, illite; C, montmorillonite with some kaolinite.

† <21 μ particle size separated by use of Bahco Micro-particle Classifier (H. W. Dietert Co.)

TABLE 2

*Mechanical analysis of soils and clays**

Diameter Limits	Vina	Sassafras	Hanford	Aiken	Bentonite	Kaolinite
mm.	%	%	%	%	%	%
2.0–1.0	3.39	1.38	3.61	1.84	—	—
1.0–0.5	6.43	5.03	16.11	2.41	—	—
0.50–0.25	14.14	30.80	25.32	2.74	—	—
0.25–0.10	18.00	32.24	19.87	4.73	—	—
0.10–0.05	10.31	6.47	9.40	5.18	—	—
0.05–0.02	13.64	9.98	10.90	13.68	0.16	1.54
0.02–0.005	12.27	6.59	6.59	18.23	46.10	38.64
0.005–0.002	6.48	2.63	2.66	11.96	16.64	26.21
0.002–0.001	4.19	0.95	1.84	8.80	8.30	12.99
<0.001	11.15	3.93	3.70	30.43	28.80	20.62

* Mechanical analysis was not performed on Egbert muck.

planchets and evaporated to dryness to drive off the acid in the solution. One gram of oven-dried soil (or 0.50 g. of clay mineral) was then placed in each beaker, brought to a 1:10 suspension with distilled water, allowed to stand 2 hours with occasional stirring, and dried at 100° C. to enhance fixation. The average activity in the planchets was taken as the dose.

Leaching methods

Each oven-dried sample was resuspended in the appropriate leaching solution, allowed to stand overnight, and transferred quantitatively to millipore filters (Type HA, Lovell Chemical Company) on Tracerlab E-8A stainless steel precipitation apparatus. For each extraction, 50 ml. of leachate was collected over a period of 4 to 6 hours. The fractions of radioisotopes leached by 50 ml. of dis-

tilled water and 50 ml. of neutral N NH_4Ac immediately after the water-leaching process are designated the "water-soluble" and "exchangeable" fractions, respectively. The fraction leached by 50 ml. of neutral N NH_4Ac without preleaching with distilled H_2O is called the "extractable" fraction. The term "fixed fraction" is applied in either case to signify the portion remaining, that is, the nonexchangeable, or the nonextractable. In the latter method, the contaminated soil was allowed to stand overnight in NH_4Ac instead of distilled water. The data presented for the "fixed" fraction were calculated by subtracting the "extractable" or the "water-soluble" plus the "exchangeable" fractions from the dose.

Radioassay methods

The entire 50 ml. of leachate was evaporated to dryness in stainless steel planchets under infrared heat lamps. The activity of the radioisotopes at equilibrium with their daughter products was determined by use of a thin mica end-window (1.8 mg./sq. cm.) G.M. tube. Counter efficiency was determined periodically with a U_3O_8 standard mounted in a similar planchet. Appropriate corrections for back-scatter, self-absorption, and isotopic decay were made where necessary.

RESULTS AND DISCUSSION

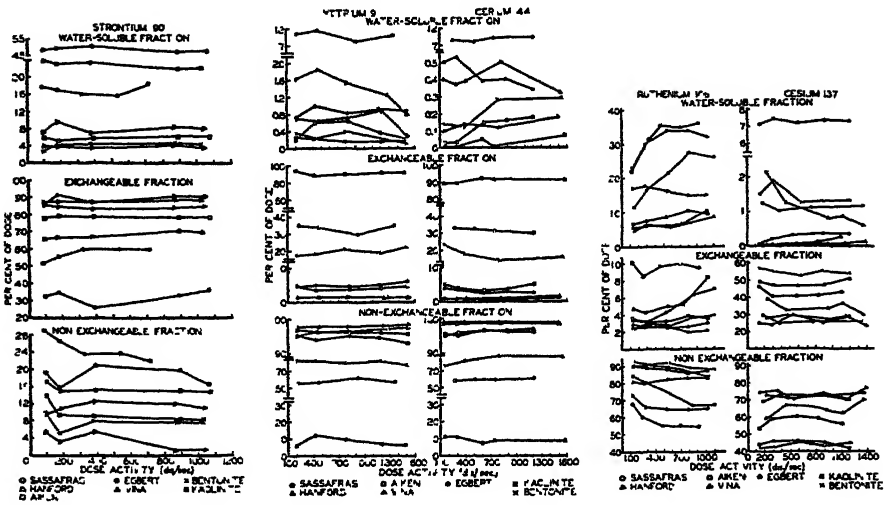
Water-soluble, exchangeable, and nonexchangeable forms of radioisotopes

The amounts of water-soluble, exchangeable, and nonexchangeable forms of radioisotopes contaminating the soils and clay minerals were determined in the dose range of 100 to 1600 dis./sec./g. soil (or 0.5 g. clay). The amount of radioisotope found in each of the three fractions increased progressively with increasing dose (fig. 1), but when the amount in each fraction was expressed as per cent of dose, it remained fairly constant over its dose range in most cases.

With few exceptions, the relative quantities of the water-soluble forms released from soils were Ru106 > Sr90 > Y91 ≥ Ce144 > Cs137. Sassafras soil and Egbert muck released much more Sr90 than Ru106. Sassafras also released larger amounts of Y91 and Ce144 than did the other soils. Hanford released more Cs137 than Ce144. The relative quantities of water-soluble radioisotopes released from bentonite were Ru106 > Sr90 > Cs137 > Y91 > Ce144. Kaolinite differed from bentonite in that it released more Sr90 than Ru106.

The relative amounts of exchangeable fractions released from soils, except Sassafras, were Sr90 > Cs137 > Ru106 ≥ Y91 ≥ Ce144. For Sassafras, the relative order was Y91, Ce144 > Sr90, Cs137 > Ru106. Like their water-soluble fractions, exchangeable Y91 and Ce144 were very much greater for Sassafras than for other soils. The exchangeable forms released from bentonite and kaolinite were Sr90 > Cs137 > Y91, Ce144 > Ru106; and Y91, Ce144 > Sr90 > Cs137 > Ru106, respectively.

As shown in figure 2, the behavior of Y91 and Ce144 conformed to their hydrolysis curves. They are soluble under strongly acidic conditions, but form colloids under alkaline conditions (4, 5). Except for water-soluble Cs137, the release of radioisotopes from Sassafras, which is acidic and predominantly



A B C

FIG. 1. WATER-SOLUBLE, EXCHANGEABLE, AND NONEXCHANGEABLE FRACTIONS OF (A) Sr90, (B) Y91 AND Ce144, AND (C) Ru106 AND Cs137 IN FIVE SOILS AND TWO CLAY MINERALS

kaolinitic, paralleled that from kaolinite. The release of radioisotopes from Aiken, which is also acidic and predominantly kaolinitic, did not correspond to that from Sassafras soil or kaolinite; this difference indicated the presence of other modifying factors, one of which may be the quantity of chemically similar elements present in the soil.

Except for Sassafras soil and kaolinite, Ru106 was released in greater amount in the water-soluble form than were the other radioisotopes. Furthermore, in contrast to other radioisotopic treatments (except Sassafras-Sr90 treatment), the water-soluble form of Ru106 was greater than its exchangeable form. This behavior of Ru106 suggested that it may have been adsorbed as an anion. To test this possibility, Ru106 extracted with 0.01N NaOH from Hanford soil, bentonite, and kaolinite was compared with that released with neutral N NH_4Ac. The amount of Ru106 liberated by NaOH was greater than that liberated by NH_4Ac, but was not great enough to warrant a conclusive statement that Ru106 was adsorbed as an anion. At least part of the increased release of Ru106 may be due to dispersion of the colloidal particles and also to the solubility of the colloids in NaOH.

Inasmuch as soils contain organic matter, the strong complexing nature of Ru[3] may also be a factor. Soil organic matter may form soluble complexes with Ru106 and thus reduce its adsorption on soil clay minerals. But complex formation does not appear to be an important factor, since bentonite, which contains no organic matter, released more water-soluble Ru106 than the other radioisotopes.

[3] Deford, D. D. The chemistry of ruthenium. 1948. (Unpublished thesis, University of Kansas. U. S. Atomic Energy Commission. Doc. NP-1104.)

The relative amounts of radioisotopes fixed in the soils (except Sassafras) were Ce144, Y91 > Ru106 > Cs137 > Sr90. For Sassafras, the order was Cs137 > Ce144, Y91, Ru106 > Sr90. The relative amounts fixed by bentonite were Ru106 > Ce144, Y91 > Cs137 > Sr90. Kaolinite fixed more Cs137 than Ce144 or Y91, but otherwise it showed similar relationships among the radioisotopes.

Considerable variations occurred in the strength by which fission products were bound to soils and clay minerals. Since soils and clay minerals differ in their physical and chemical properties, their fixation of fission products apparently is influenced by the interplay of many factors.

Effect of pH of leaching solution

The pH of leaching solutions may have a great influence on the extractability of certain adsorbed cations from exchange complexes. To test the effect of pH, leaching solutions were prepared by titrating acetic acid to various pH levels (pH 2.3 to 9.2) with NH_4OH in such a way that the acetate concentration was always 1 mole. Hanford sandy loam was used as the test soil. Within the range studied, the extractability of Sr90 was approximately constant (fig. 2). The extractability of Cs137 tended to decrease slightly as the pH increased above pH 3.5, but below pH 3.5 it decreased very sharply. A similar effect was observed by using Sassafras soil, and by using 0.04 N HNO_3 on Hanford soil. This

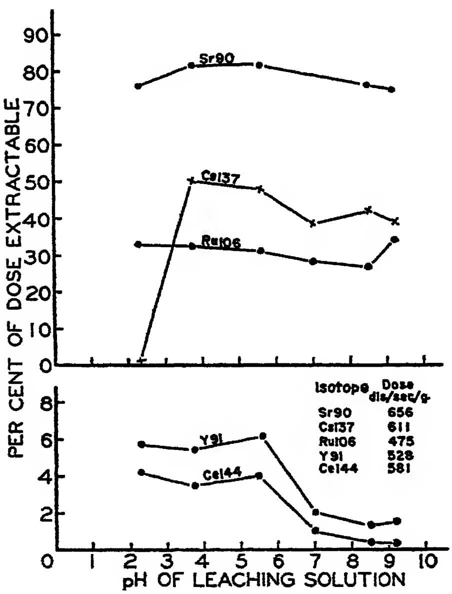


Fig. 2

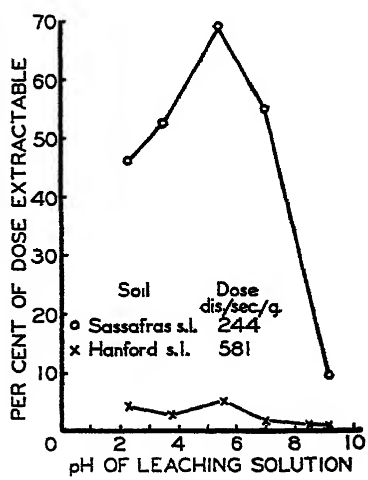


Fig. 3

Fig. 2. Influence of pH of Leaching Solution on Extractability of Various Radioisotopes in Hanford Sandy Loam

Fig. 3. Influence of pH of Leaching Solution on Extractability of Ce144 from Two Soils

decreased extractability of Cs137 appears to be a function of pH, but the mechanism is not understood. The extractability of Ru106 decreased slightly with increasing pH up to 8.5 and then tended to rise.

The amount of Y91 and Ce144 released was fairly constant with increasing pH up to about 5.5, but above this pH level it decreased sharply. Certain investigators (4, 5, 8) have shown that a notable decline in the solubility of Y91 and Ce144 occurs with increasing pH because of the formation of colloids. The present effect with Y91 and Ce144 in soil may well be the same phenomenon. Apparently, the pH of the leaching solution has great influence on the amount of these rare-earth elements extracted.

The effect of the pH of the leaching solution depends on soil type (fig. 3). At pH 5.4 Sassafras soil released approximately 18 times as much extractable Ce144 as did Hanford. Figure 1B demonstrates that kaolinite fixed much less Ce144 in the nonexchangeable form than did bentonite. The very large amount of Ce144 released by Sassafras as compared to Hanford soil is probably due to the predominantly kaolinitic character of the Sassafras soil and, as shown subsequently, to its acidic reaction. The Hanford soil, on the other hand, is illitic and only slightly acidic.

Effect of acid pretreatment on extractability of Sr90 and Cs137

When contaminated bentonite or kaolinite was leached with 0.04 N HNO_3 all the radioisotopes studied (except Ru106) were liberated in considerably lesser amounts than by neutral N NH_4Ac (kaolinite, 23 to 50 per cent; and bentonite, 48 to 82 per cent less, depending on the radioisotope). The lesser release of radioisotopes by 0.04 N HNO_3 was considered due to the lower ionic concentration of the leaching agent, since by leaching contaminated bentonite with N HNO_3, all radioisotopes were released in greater amounts than by NH_4Ac; Strontium 90, Y91, and Ce144 were displaced completely. The release of Cs137 and Ru106 was increased from about 11 and 32 per cent to 90 and 85 per cent, respectively.

The clay minerals leached with 0.04 N HNO_3 should continue to liberate more radioisotopes when subsequently leached with NH_4Ac. Table 3 shows that this

TABLE 3

Effect of acid pretreatment of bentonite on the replacement of Sr90 and Cs137 by ammonium and hydrogen ions

Radioisotope	Dose	First Leaching Solution*	First Leaching	Second Leaching Solution*	Second Leaching	Total Amount Leached
	dis./sec./0.5 g.		*% of dose*		*% of dose*	*% of dose*
Sr90	4.45×10^4	HNO_3	46.0	NH_4Ac	48.0	94.0
	4.45×10^4	HNO_3	46.6	HNO_3	6.1	52.7
Sr90	4.3×10^4	HCl	58.0	NH_4Ac	40.6	98.6
	4.3×10^4	HCl	55.4	HCl	6.4	61.8
Cs137	8×10^3	HNO_3	13.2	NH_4Ac	47.0	60.2
	8×10^3	HNO_3	12.8	HNO_3	9.4	22.2

* Leaching solutions were 0.04N HNO_3, 0.04 N HCl, and neutral N NH_4Ac.

TABLE 4

Effect of acid pretreatment of bentonite on water-soluble and exchangeable Cs137 and Ce144

Radioisotope	Dose	Pretreated (pH 4.3)		Untreated (pH 8.0)	
		Water-soluble	Exchangeable	Water-soluble	Exchangeable
	dis./sec./0.5 g.	*% of dose*	*% of dose*	*% of dose*	*% of dose*
Cs137	182	1.0	82.7	1.6	56.5
Ce144	182	0.35	87.5	0.13	22.2

does occur. In this experiment, six 0.5-g. samples of bentonite were leached with 50 ml. of 0.04 *N* HNO_3 or HCl. After this acid treatment, three of the samples were leached with 50 ml. of NH_4Ac, whereas the other three were leached with an additional 50 ml. of HNO_3. The initial leaching of the Sr90-treated bentonite with HNO_3 released 46 per cent of the dose. The samples followed with NH_4Ac leaching released an additional 48 per cent of dose, but the continued leaching with HNO_3 released only an additional 6 per cent. A similar effect was observed by using HCl instead of HNO_3. Although much less Cs137 than Sr90, was released in the pretreatment step, the effect of greater additional release of adsorbed radioisotope with NH_4Ac was also obtained in the case of Cs137. The total recovery of Sr90 or Cs137 was approximately the same whether or not the NH_4Ac leaching was preceded by acid leaching. Apparently, preleaching with 0.04 *N* acid had only slight, if any, effect on the release of nonexchangeable Sr90 and Cs137.

In these experiments, the radioisotopes were added to bentonite before leaching with acid. If the process is reversed, that is, if the bentonite is treated with acid before it is contaminated, the adsorbed radioisotopes are released more readily. This was demonstrated by making H-bentonite from natural bentonite (pH 8). The H-bentonite was then titrated to pH 4.3 with NaOH, oven-dried, and carried through the leaching procedure. As shown in table 4 the pretreated bentonite released considerably more exchangeable Cs137 and Ce144 than did the untreated clay. The water-soluble form of Ce144 also increased, but that of Cs137 decreased for an unexplained reason. From these data, it can be concluded that the hydrogen ion is more strongly adsorbed than is Cs137 or Ce144. On the basis of pH *per se*, more of these radioisotopes should be released from acid soils than from those of neutral or alkaline reaction. The effect observed here may explain, in part, why the water-soluble fractions of radioisotopes released from Sassafras were much greater than from other soils, since Sassafras showed much higher hydrogen-ion saturation (92 per cent) of its exchange complex than did the other soils.

Distinctions between water-soluble, exchangeable, and nonexchangeable forms of radioisotopes

Separation of the radioisotopes into water-soluble, exchangeable, and nonexchangeable forms is empirical, and there is a practical distinction. With potassium, the exchangeable form has been shown to represent a rather definite frac-

TABLE 5

Sr90 and Cs137 leached from Hanford sandy loam by water and ammonium acetate*

Leachate Fraction	Sr90		Cs137	
	Water-soluble fraction	Exchangeable fraction	Water-soluble fraction	Exchangeable fraction
ml.	*% of dose*	*% of dose*	*% of dose*	*% of dose*
0–30	7.17	79.55	0.39	33.7
0–40	9.03	80.15	1.09	37.5
0–50	9.76	81.09	1.01	38.9
50–60	0.78	0.53	0.24	0.73
60–70	0.54	0.27	0.18	0.58
70–80	0.72	0.25	0.23	0.52
80–90	0.57	0.15	0.21	0.46
90–100	0.74	0.17	0.08	0.33

* Dose: Sr90, 568 dis./sec /g ; and Cs137, 975 dis./sec./g.

tion of the total soil potassium (1, 2, 7). Because radioisotope techniques are more sensitive than chemical methods, the distinction among the various fractions was not so sharp in the present experiments as in the potassium experiments (1). This is shown in table 5, which presents the percentages of the water-soluble and exchangeable fractions of Sr90 and Cs137 recovered from Hanford sandy loam with increasing amounts of leachate.

Approximately 74 and 98 per cent of the Sr90 activity leached by 100-ml. portions of water and NH_4Ac, respectively, were found in the first 50 ml. of leachate. With Cs137, the recovery of water-soluble and exchangeable fractions in the first 50 ml. was about 51 and 94 per cent, respectively. The distinction of the various fractions was better for Sr90, which showed much less fixation than did Cs137. Repeated leaching with NH_4Ac after collection of 50 ml. of leachate yielded decreasing but detectable quantities of both radioisotopes. This effect indicates that the nonexchangeable form of radioisotope was slowly converted to the exchangeable form, which in turn slowly became water-soluble.

Recovery of radioisotopes carried through leaching procedure

The reliability of the data presented here depends on the recovery of the radioisotopes used as well as the assignment of any losses accruing. To this extent, a careful effort was made, each of the radioisotopes being carried through the leaching procedure in absence of any soil or clay mineral. The recovery of Sr90, Y91, and Ce144 (99.5 $\pm$ 3 per cent) proved to be all but complete. For Cs137 and Ru106, there were losses of 20 and 32 per cent, respectively. This procedure was repeated with Cs137 and Ru106, but with the addition of Hanford sandy loam. Here the loss of Ru106 was reduced to only 4 per cent whereas that of Cs137 was much less, or about 0.4 per cent (table 6). Apparently, there was a preferential adsorption of these radioisotopes on the soil. The recoveries of the added radioisotopes were also checked in each case by summing the amount of isotope recovered in the water-soluble, ex-

TABLE 6

Loss of Cs137 and Ru106 carried through the leaching procedure*

Treatment	Cs137	Ru106
	% of dose	*% of dose*
Loss without soil		
In mixing beaker	17.7	21.3
On Millipore filter	2.7	10.7
Total	20.4	32.0
Loss with soil†		
In mixing beaker	0.3	3.8
In Millipore filter	0.1	0.4
Total	0.4	4.2

* Dose: Cs137, 204 dis./sec.; and Ru106, 716 dis./sec.

† Hanford sandy loam.

changeable, and nonexchangeable fractions. In terms of the treatment with which this paper deals, in presence of soils or clay minerals, loss due to adsorption on apparatus is minimal and within the limits of experimental error.

SUMMARY

Water-soluble, exchangeable, and nonexchangeable forms of long-lived and medium-lived fission products (Sr90, Y91, Ru106, Cs137, and Ce144) contaminating five soils and two clay minerals were studied by the use of leaching procedures.

With few exceptions, the relative relationships of these fission products in the soils were:

Water-soluble fraction: Ru106 > Sr90 > Y91 ≥ Ce144 > Cs137

Exchangeable fraction: Sr90 > Cs137 > Ru106 ≥ Y91 ≥ Ce144

Nonexchangeable fraction: Ce144, Y91 > Ru106 > Cs137 > Sr90

Exceptions were discussed on the basis of soil pH, chemical properties of radioisotopes, and clay mineral type.

The relative relationships of the radioisotopes in the clay minerals were:

Water-soluble fraction: bentonite; Ru106 > Sr90 > Cs137 > Y91, Ce144
kaolinite; Sr90 > Ru106, Cs137 > Y91 > Ce144

Exchangeable fraction: bentonite; Sr90 > Cs137 > Y91, Ce144 > Ru106
kaolinite; Y91, Ce144 > Sr90 > Cs137 > Ru106

Nonexchangeable fraction: bentonite; Ru106 > Ce144, Y91 > Cs137 > Sr90
kaolinite; Ru106 > Cs137 > Y91, Ce144 > Sr90

In comparison with the other radioisotopes, Cs137 and Ru106 were fixed in relatively large amounts by kaolinite. Bentonite pretreated with dilute acid showed

less adsorption of Cs137 and Ce144 than did untreated bentonite, which indicates that the hydrogen ion is more strongly adsorbed than are these ions.

The pH of the leaching solution had great effect on the release of Y91, Cs137, and Ce144.

In the competitive adsorption between the soils and clay minerals and the Pyrex glass of the container, the radioisotopes showed a decidedly greater preference for the soils and clay minerals.

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PROBLEMS OF SOIL NOMENCLATURE—A REVIEW OF *'Multilingual Vocabulary of Soil Science'*

H. C. MOSS

University of Saskatchewan[1]

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A critical examination of some of the definitions in *Multilingual Vocabulary of Soil Science*[2] reveals some of the problems of soil nomenclature, including those related to soil classification. The Preface to this publication expresses the hope that the "work will assist in the international exchange of information on soils, and will lead to a greater correlation and uniformity of soil descriptions." Regional groups of soil workers could further this purpose of the *Vocabulary* by a study of the publication as it pertains to their individual regions and concepts of soil formation and classification. In the following discussion, Saskatchewan workers report such a study.

In a review of the English-language section of the *Vocabulary*, the attention of these workers has been focused on those definitions that appear to be either inadequate or incorrect. Only definitions from the fields of soil classification and morphology were considered; no attempt was made to review other aspects of soil science. In the interest of constructive discussion, modifications and additions to definitions are suggested. In some instances a new definition, which indicates more clearly the concept of Saskatchewan workers, is presented. Each definition is identified by the section and number of its position in the original publication.

That everyone will agree with the criticisms and suggestions expressed in the following pages is not to be expected. But if by the discussion the need for more work on the problems of soil nomenclature, and particularly for more cooperation among the various English-speaking groups of soil scientists, is emphasized, its main purpose has been accomplished. There is a great danger that the English-language definitions of the *Multilingual Vocabulary of Soil Science* will be assumed to represent the viewpoint of all English-speaking groups. Although the F. A. O. list does provide a good starting point for the development of a soil nomenclature, no generally satisfactory list of definitions can be achieved without considerable further study.

B. Texture and Structure

B17. "Structure: Arrangement of soil particles into aggregates." Is this definition adequate? It appears to be more suitable as a definition of aggregation. It is suggested that a statement should be added to the effect that structural aggregates occur in a variety of recognized shapes and sizes.

It is also noted that Section B does not contain definitions for columnar, prismatic, platy, nutty, or blocky structures.

[1] Saskatchewan Soil survey.

[2] G. V. Jacks, Editor. *Multilingual Vocabulary of Soil Science.* Food and Agriculture Organization of the United Nations, 1954.

H. Soil Formation and Morphology

H10. "Degradation: Change in soil due to increased leaching." Would the leaching of salts from a solonchak be regarded as soil degradation? It is suggested that degradation is more commonly associated with changes which are regarded as forming a less desirable agricultural soil, as in the progressive podzolic leaching of a chernozem. The definition in French implies this concept of degradation, and perhaps the term should be restricted to this practical meaning.

L. Soil Classification

L8. "Great soil group: A taxonomic group of soils containing one or more families." This definition appears to be both inadequate and incorrect. It is inadequate because it contains no concept by which a great soil group may be recognized; it is incorrect in introducing the term "family" into the definition. The great soil group was recognized before the family was established. For regions where the family is not yet established, the definition is meaningless.

It is suggested that a definition of "great soil group" include some reference to soil genesis, since all soils belonging to a given great soil group should belong to one kind or type of formation. For example, "great soil group" might be defined as a group of soils whose principal morphological features indicate that these soils belong to the same genetic type or kind of soil formation.

L9. "Family: A taxonomic grouping of similar soils intermediate between series and great soil group." The term "intermediate" requires a more precise definition. Since the family is usually composed of several different series or their equivalents, the term "similar soils" likewise requires further definition. Such soils cannot be similar in all characteristics.

L6. "Intrazonal soil: Well-developed soil whose morphology reflects the influence of some local factor of relief, parent material or age rather than of climate and vegetation." This definition prompts the question: Can there be a "well-developed" soil which does not reflect, to some degree at least, the influence of climate?

It is suggested that the definition of intrazonal soil indicate that the influence of climate and vegetation is less pronounced than the influence of some other soil-forming factor. The definition in French implies this concept.

It is further suggested that the term "intrazonal soil" could very well be dropped. Experience has shown that it is not an essential unit of classification; in fact, attempts to use it in this region caused more trouble than its ultimate rejection.

M. Organic and Peat Soils

M4. "Bog soil: Peaty soil with surface peat deeper than about 16 cm. . . ." What is the basis for selecting such a thin peat layer? By this definition many half-bog soils (M 5) will have to be reclassified as bog soils. It is suggested that both of these soils require new definitions—and preferably new names. For example, organic (bog) soil might be defined as a poorly drained soil whose major horizons consist of peaty material contaning more than 30 per cent organic matter. To such a definition could be added a specified thickness of peat, when such is agreed upon.

M7. "Tundra soil: Dark-colored soil with highly organic surface horizon and a frozen subsoil." This definition would equally well characterize many grassland soils of western Canada during the winter months. It is suggested that for tundra soils, some reference be made to permaforst.

N. Podzolic Soils

N2. "Podzol: Soil with acid-humus horizon overlying B horizon of iron-oxide or iron-oxide and humus accumulation." There is no reference in the definition to an important characteristic, the bleached A_2, of most podzol types.

N4. "Grey-brown podzolic soil: Forest soil with thin A_0 and A_1 over a greyish-brown leached A_2 and brown blocky B horizon." Is the A_0 an important characteristic of this soil? Much of the literature suggests that the A_0 is usually absent. A more important characteristic of the gray-brown podzolic profile is the heavier textured or clayey B, but this is not mentioned in the definition.

N5. "Grey wooded soil: Soil with thin A_1, thick grey A_2 and greyish-brown blocky B horizons, commonly over calcareous parent material." This English-language definition omits two of the most important characteristics of this soil: the very heavy textured or clayey B horizon, and the presence of an A_0 horizon. Furthermore, the A_1 is frequently absent and in any event is not an important feature of this profile. It is a matter of opinion whether the typical structure of the B horizon should be described as "blocky."

It is suggested that the gray wooded soil might be defined as follows: Forest soil with A_0, thick, gray A_2, and illuviated B horizons with accumulations of clay and sesquioxides, occurring on parent materials of high base status.

O. Gley and Meadow Soils

O4. "Gley soil: Soil with high ground water and iron-oxide accumulation in the region of the water table." Most of the literature dealing with this soil emphasizes the presence or effect of reduced iron, a factor mentioned in the French-language definition of glei soil. Furthermore, the definition of glei (I 14) also makes reference to reduction of iron. These facts suggest that further work is required before satisfactory concepts and definitions of gleiing, gleied horizons, and glei soil can be adopted.

P. Arid and Semiarid Soils

This section includes chernozem, degraded chernozem, black earth, and prairie soils, which range climatically from subhumid to humid conditions. In this respect the title of the section is misleading. A better title might read: Chernozemic and Other Soils of Grassland Regions, in which case it is suggested that degraded chernozem be placed with the podzolic soils.

P 1. "Chernozem: Dark, well-drained grassland soil, granular and rich in humus to some depth, with or without concentration of clay in the B horizon, and calcareous below." The phrase "rich in humus to some depth" is too vague; why not "with humus-rich A_1 horizon"? No reference to clay concentration is required, since such concentration may be either present or absent. Finally, the term "cal-

careous below" is not accurate, since lime carbonate may be present in the upper horizons of some chernozemic soils.

P 2. "Degraded chernozem: Dark, well-drained soil of grassland–forest transition, with a greyish A_2 horizon." The definition omits an important characteristic of this soil, that is, the development of podzolic features, including the A_0 horizon and the illuviated B horizon. The latter horizon is likely to have an accumulation of clay. A suggested definition of degraded chernozem might be: Former grassland soil undergoing podzolic leaching, and having A_0, dark A_1, gray A_2, and illuviated B horizon.

P 8. "Chestnut soil: Dark brown over lighter colored soil overlying a calcareous horizon." The definition makes no reference to grassland environment or to humus content of the A horizon.

P 9. "Brown (steppe) soil: Brown to light brown nearly neutral soil, usually overlying a calcareous horizon." Again no reference is made to the organic matter content of the A horizon. The expression "nearly neutral" does not apply any more specifically to brown than to dark brown or chernozem soils.

It is suggested that the definitions of chernozem, chestnut, and brown soils should indicate that all these soils are developed under grassland vegetation, and that their differentiating characteristics are mainly due to climatic differences which are reflected in the range of colors and associated humus contents of the A_1 horizons. For example, chernozem might be defined as grassland soil developed on calcareous parent material, with well-developed A_1 horizon whose very dark color is associated with a high content of humus.

Q. Saline and Alkali Soils

Q 1. "Saline soil: Soil whose properties have been determined by the presence of salts." The definition as it stands represents an impossible situation. The properties of a soil cannot be determined by one factor. Texture is one of the properties of a soil and it is not primarily determined by "presence of salts." The definition omits reference to soil drainage, to kind and amount of salts, and the important fact that saline soils are characterized by the presence of *soluble* salts.

It is suggested that saline soils be described as poorly drained soils further characterized by the presence of soluble salts of the alkalies and alkaline earths in concentrations in excess of those associated with the regional well-drained soils.

Q 2. "Solonchak: Saline soil without structure." "Without structure" should be altered to "without marked horizon development and differentiation." Actually solonchaks may possess well-developed granular structures.

Q 3. "Solonetz: Formerly saline soils from which the salts have been leached, with cloddy prismatic or columnar structures." The definition implies that the salts are completely removed from the profile, which is not a common condition in the solonetz. It would also seem desirable to make some reference to alkaline reaction and to the presence of sodium.

The following definition is offered as a more specific description of solonetz: Soil with partially leached A horizon and fine-textured prismatic or columnar-

structured B horizon, and associated with highly alkaline reaction, dominance of exchangeable (magnesium plus sodium) and saline parent materials.

Q 4. "Solod (soloth): Leached saline soil (degraded solonetz) having a pale A_2 horizon and a degraded fine-textured B horizon." The definition does not mention the acid reaction of the leached horizons or the fact that the thick A_2 has extended into the former solonetzic B horizon.

S. Intrazonal and Azonal Soils

S 4. "Secondary soil, transported soil: Soil formed on transported material." If a soil formed on transported material is the first soil to develop at that site and on that material, it seems absurd to call it a secondary soil. The term "transported soil" is not only absurd, it is impossible. The same may be said of residual soil (S 5), which is defined as *"Soil resting on the material from which it was formed."* This should read "Soil resting on material similar to that from which it was formed."

The difficulty of using the terms "secondary" and "transported" is illustrated by reference to a soil formed on thick, uniform, glacial lacustrine sediments. Since this soil is formed on transported material it is a secondary or transported soil, but, since it rests on material similar to that from which it was formed, it is also a residual soil. It is suggested that these terms, borrowed from geology, be dropped from the vocabulary of soil science.

S 11. "Planosol: Intra-zonal soil having a sharply delineated clay pan or hardpan arising from cementation, compaction, or high clay content; formed under forest or grassland vegetation in mesothermal to tropical perhumid to semi-arid climates, usually but not always with fluctuating water table." This is one of the longest definitions of a soil in the publication, but its length is probably necessary because planosol comprises a group of diverse soils with a single common feature, that is, the presence of "a sharply delineated clay pan or hardpan." The practise of classifying soils on the basis of a single characteristic is of questionable value except for agronomic or other practical purposes.

The Agricultural Regions of the United States. By LADD HAYSTEAD AND GILBERT C. FITE. The University of Oklahoma Press, Norman, 1955. Pp. 288. Price $4.00

After considering the "non-existent typical American farm," the authors proceed with analyses of the agriculture of 11 production regions. Colorful and explanatory designations for these regions include: land of abandonment; prime market; intensive region; reorganizing belt; shifting cotton belt; feedbag of democracy; dairyland; American granary; far distances and dry skies; farm in the sky; and land of tomorrow. Since one state may be included in more than one region some overlapping occurs. The central theme is the dynamic quality of agriculture, for which the machine is responsible, with a prophecy of even greater change ahead. Thus the book is of great interest today, although it may be badly outdated by 1975, or even before. The authors admit that farming is something more than dollars and cents, and that farmers farm because they want to. The book is well illustrated, attractively written, and its pronouncements merit study.

Can We Solve the Farm Problem? By MURRAY R. BENEDICT. The Twentieth Century Fund, New York, 1955. Pp. 601. Price $5.

The author analyzes the report of a Committee on Agricultural Policy appointed by the Fund to analyze federal aid to agriculture. The Committee's report is appended as the 12th and last chapter of the volume. Two members of the Committee issue a supplementary statement indicating points of disagreement with the other 10 members. Soil-plant scientists will be particularly interested in chapter 9, which develops the history of the soil conservation movement and indicates something of its costs and accomplishments. The author points out that the present (1953) national outlay for conservation activities—including $60 million for the Soil Conservation Service, $270 million for the conservation payment program, $10 million for the Bureau of Land Management, $225 for the Bureau of Reclamation, $350 million for the Army Corps of Engineers for flood control, and $6 million for flood prevention activities—totals around $1 billion. Much of this expense has been justified by the accomplishments, but the author thinks that the conservation payment program should now be largely eliminated. The minority report suggests that too little attention is paid to crop surpluses; that production is increasing more rapidly than population; that a program to improve diets and increase consumption both at home and abroad is needed; and that effective and quick relief for farmers is necessary. This is a first-class discussion of the farm problem.

Chapingo. Directed by FIACRO MARTINEZ MORTINEZ. Escuela Nacional de Agricultura, Chapingo, Mexico, 1955. Pp. 40. Annual subscription $25 M.M.

Chapings is the organ of the Escuela Nacional de Agricultura, of which the present (January-February 1955) issue is vol. 8, no. 49. This number contains

articles on temperature correlation with altitude, latitude, and precipitation; on cultivation of cotton, with special reference to pest control; on agricultural machinery (tractors), sugar cane pests, and the polders of Holland. It also contains a glossary of botanical terms. Photographs of "*nuevos ingenieros*," with the subjects of their theses, are an attractive additional feature.

The Cytology and Life-History of Bacteria. Second Edition. By K. A. Bisset. The Williams and Wilkins Company, Baltimore, 1955. Pp. 164, figs. 65. Price $6.

The author, a reader in systematic bacteriology, University of Birmingham, deals with theories of cytological structure and techniques in obtaining necessary corroborative evidence. He points out that bacteria are best examined in water-mounted preparations and not in dried, fixed smears, and describes his techniques in considerable detail. The several other chapters present clear pictures of surface structures, nucleii, reproductive processes, sexuality, life-cycles, macroformations, and evolutionary relationships in bacteria. The final chapter concerns genetic confirmation of cytology and sources of the evidence. The author concludes that there is "little to suggest that the entire, complex pattern of bacterial dissociation may not be explicable in terms of multiple and interrelated gene changes." A bibliography is appended to each chapter. The illustrations are especially noteworthy. This is an excellent presentation of the subject, and the book itself is a work of art.

Experimental Design. By Walter F. Federer. The Macmillan Company, New York, 1955. Pp. 544. Price $11.

The author is professor of biological statistics at Cornell University, and his book an outgrowth of a series of lectures at the Geneva, New York, Agricultural Experiment Station in 1948–49. He has endeavored to assemble the material needed for a college course, with comprehensive coverage of design of experiments and analysis of data obtained from them. By eliminating some of the chapters, as the need arises, he visualizes use of the book at several levels of instruction. But the student had better have a good understanding of mathematics and statistics before he undertakes to master the contents of this volume. Such matters as plot technique, randomization, factorial experiments, compounding, incomplete data, and covariance are dealt with in detail. A bibliography of 340 references and lists of problems for clarification of the text are appended. The book represents a tremendous amount of work on the part of the author, and his effort and accomplishment merit recognition.

Experimental Program in Brazil. By J. C. Medcalf, W. L. Lott, P. B. Teeter, and L. R. Quinn. IBEC Research Institute, New York, 1955. Pp. 59.

This bulletin reports studies in mulching, irrigating, trace elements, foliar analysis, and climatic factors as they are related to coffee production in Brazil. It also deals with brush, weed, and Bermuda grass control, and soil fumigation in coffee. The most spectacular feature of the report concerns the effects of chelated forms of copper, manganese, iron, and zinc on coffee yields, which were greatly increased by their use at the rate of 28 pounds a tree.

Magnesia, der fünfte Pflanzenhauptnährstoff. By A. Jacob. Ferdinand Enke Verlag. Stuttgart, Germany, 1955. Pp. 127, figs. 10, plates 8. Price DM 19.

This is an excellent review of the subject, with 419 references and 8 color plates showing symptoms of magnesium deficiency in nine important crops, in fruit, and in vegetable plants. The 12 chapters deal with the chemical properties of magnesium; amounts in plants; symptoms of deficiency in 34 plants—including grasses, legumes, tubers, grains, fruits, roots, vegetables, and forest trees; ion antagonisms; functions; importance for animals; amounts in soils of Germany and various other countries, including the United States; experimental tests; as constituent of fertilizers; and some conclusions. As might be assumed, the fourth element is calcium. This is the best developed presentation of the magnesium problem that has come to our attention.

Man and the Winds. By E. Aubert de la Rue. Philosophical Library, New York, 1955. Pp. 206. Price $6.

Madge E. Thompson translated this book into English, omitting some passages of purely local interest in France and adding a few notes of general interest. The 18 chapters outline the various types of winds and their effects on climate and dwelling needs; their eroding action when carrying sand and soil; their use as sources of energy for manufacturing, lighting, and sailing; their relationships to aviation; and their control by vegetative barriers. The last chapter deals with legend and mythology. The book is well illustrated, with more than 100 two-item plates. A bibliography of 74 references is appended. The author concludes that "wind is a friend of man," but a "friend to be feared whose benefits are dearly bought." This is a highly interesting book.

The North American Midwest. Edited by John H. Garland. John Wiley and Sons, Inc., New York, 1955. Pp. 252, figs. 80. Price $8.

Fifteen geographers of the Midwest participated in the writing of the 16 chapters in this book. They divide the eastern half of the United States into the East, the Midwest, and the South. The Midwest itself is divided into 10 units of which the West-Central area is designated as having contributed most to the significance of this region, which includes southwestern Minnesota, most of Iowa and northern Missouri, central Illinois, and a part of northwestern Indiana. Called "the epitome of modern agricultural production," the best of this land was settled last because it was wet and had few trees. In general, the industrial and population centers of the entire region are to the east and the agriculture to the west. The several authors consider problems of agriculture, industry, transportation, trade, and population, with particular reference to urban and rural patterns. They emphasize the fact that this is a region of especially cold winters and hot summers. A selected bibliography is appended.

On the Nature of Man. By Dagobert D. Runes. Philosophical Library, New York, 1955. Pp. 105. Price $3.

The author, a graduate of the University of Vienna and former director of the Institute for Advanced Education, begins his discourse with the statement that

"man is as little the final purpose of divine providence as an elk, or a beetle, or a salamander"; man will make "his own hells and heavens, as will other animals, and feel himself cock of the evolutionary roost." The history of man is traced with his gods, his alphabet, his laws, his wars, and his tryannies, to a final chapter, "Evening Thoughts," which contains approximately a hundred pithy, isolated thoughts about man that place him somewhat lower than the angels, and considerably lower than he would place himself, for example: "thinking is a luxury of the mind; most people stick to the necessities."

Our Daily Poison. By LEONARD WICKENDEN. The Devin-Adair Company, New York, 1955. Pp. 178. Price $3.

The subtitle of this book is "The effects of DDT, fluorides, hormones, and other chemicals on modern man." Many persons will be greatly disturbed on reading this volume, partly because the defending scientists, who were called before the House Investigating Committee under the chairmanship of Congressman Delaney, made a surprisingly poor case for the defense. And no good defense can be made for some of the currently used chemicals and for certain methods of their use. Problems arising from the use of agricultural pesticides and of food and feed additives must be dealt with constructively, and it is extremely doubtful that this book accomplishes that purpose.

Science and Modern Life. By E. JOHN RUSSELL. Philosophical Library, New York, 1955. Pp. 101. Price $2.75.

The author, formerly director of the Rothamsted Experimental Station, begins with a discussion of the controversy between the early scientists and the theologians and among the theologians themselves. The book covers the development of geologic and evolutionary concepts, growing rate of application of the sciences, rapid exhaustion of natural resources, increasing leisure and longevity, growing world population, ever-greater complexity of our social problem, possibilities ahead with nuclear energy, thought control of tyrannical governments, and the misuse of scientific discoveries. In the final pages, the discussion returns to the conflict between science and religion and concludes that young people of today "are faced with the problem of ensuring that, in gaining control over Nature, man does not lose his own soul."

So Bold an Aim. By P. LAMARTINE YATES. Columbia University Press, New York, 1955. Pp. 174. Price $1.50.

The author outlines the progress that has been made during 10 years of "international cooperation toward freedom from want" by the Food and Agriculture Organization of The United Nations. A member of the staff from its inception, he points out that "many are pessimistic as to the capacity of the under-developed countries to climb out of primary poverty and, capacity apart, as to the possibility of their doing so," and comments that "it may, however, be pertinent to enquire what the outlook was in Europe 200 years ago when she started pulling herself up by her bootstraps." On the concept that "international institutions

are a waste of taxpayers' money," he points to the challenge of malnutrition, the need for technical assistance, the Point-Four Program and its accomplishments, and some of the frustrating aspects of the problem. He concludes "that an agency like FAO, with all it stands for and all the services it provides, will be wanted more and more."

Soil Physics. Third Edition. By L. D. BAVER. John Wiley and Sons, Inc., New York, 1956. Pp. 489, figs. 105. Price $7.75.

The author, director of the Hawaiian Sugar Planters Association Experiment Station, dedicates his book to Guy W. Conrey, Marion J. Funchess, and Merritt F. Miller, which indicates an association in his formative years with the agricultural experiment stations of Ohio, Alabama, and Missouri. The book has been greatly improved in this third edition. The material is presented in 12 chapters dealing with soil as a disperse system, its mechanical composition, soil-water relationships, structure, air, water, irrigation, drainage, temperature, tillage and erosion. For the most part the presentation is nonmathematical and the language clear and lucid. There is evidence of many years of earnest thought and of wide and careful reading in this field, reinforced by a practical knowledge of the subject. Designed for advanced undergraduates and for graduate students, this volume is the best modern presentation on soil physics available in this country and, probably, in the world.

The Sugar Beet and Its Manuring. ANONYMOUS. International Potash Institute, Berne, Switzerland, 1955. Pp. 74. Paper bound.

This interesting brochure gives statistics of the sugar industry, indicates how sugar beets fit into the farm economy, outlines conditions best suited for their production, discusses their nutrient requirements, offers suggestions on fertilizers for sugar beets, and describes and illustrates signs of deficiency of nitrogen, phosphorus, potassium, manganese, boron, calcium, and magnesium. Some useful data are appended.

Wording en Opbouw van de Wieringermeer. ANONYMOUS. H. Veenman and Zonen, Wageningen, The Netherlands, 1955. Pp. 805, figs. 177.

This book has to do with the origin and development of the Wieringermeer polder, with a review of the reclamation and colonization of the first polder. A 64-page summary in English and some 150 references are appended. The legends for the illustrations, many of which are highly interesting and instructive, are given in both Dutch and English. Reclamation of land was necessitated by the ever-greater inroads of the North Sea, which reached its peak about 1395. First attempts to reclaim some of this submerged area were not very successful, but in 1852 success was attained with some 40,000 acres. As a result, the Zuiderzee Committee was founded in 1886 and its deliberations were responsible for enabling legislation in 1918. More than 500,000 acres of land have now been reclaimed, and a fresh water lake has been developed in the center of the area. The results of the researches concerned with the origin and correction of soil

acidity, conversion of sodium clay into calcium clay, meeting fertilizer needs, inoculating legumes, subirrigating, and developing cropping systems are presented in detail. A highly important book that merits study.

Yearbook of Food and Agricultural Statistics, vol. 8, part 1. Edited by B. Tumlir. Columbia University Press, New York, 1956. Pp. 411. Price (hard cover) $3.50.

This yearbook covers by countries land resources, uses, and irrigation, population, 50 crops, livestock, food supply, means of production (including fertilizers and pesticides), prices, and index numbers. The material is presented in English, French, and Spanish. World population for 1953 is estimated at 2,508,000,000, in comparison with an estimated 2,295,000,000 in 1937. Excluding the USSR, world consumption of nitrogen for 1953–54 is estimated at 5,300,000 metric tons, that of phosphoric acid at 6,500,000, and that of potash at 5,200,000.

The Editors

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FATE OF LABELED NITRATE AND AMMONIUM NITROGEN WHEN APPLIED TO GRASS AND CLOVER GROWN SEPARATELY AND TOGETHER

T. W. WALKER, A. F. R. ADAMS, AND H. D. ORCHISTON

Canterbury Agricultural College, New Zealand[1]

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In New Zealand, clovers are relied on as the primary source of the large amount of nitrogen needed for high pasture production; under the best climatic conditions improved strains of white clover may fix as much as 600 pounds N per acre per annum. In developing general principles in a recent discussion (19, 20) on the nitrogen economy of grass-legume associations and the nitrogen cycle in grassland soils, it was assumed that clovers take up little if any combined N when grown in association with grasses. The main objective of the present experiments was to test this assumption. Evidence (19) also suggested that grasses may utilize all the combined N (available from the soil or applied as fertilizer), about two thirds being recovered in the tops and the other third retained either in the roots or by microorganisms. As a corollary of this, the losses of N by denitrification or leaching from grassland soils were small under normal field conditions. This earlier work also suggested that clovers, under certain ill-defined optimal conditions, may transfer underground to associated grasses about half the nitrogen they fix symbiotically. It was hoped that the present trials would also provide further information on some of these points.

EXPERIMENTAL

Grass (pedigreed Italian ryegrass) and clover (New Zealand pedigreed white clover) were sown separately and together in pots. Two forms of labeled nitrogen [KNO_3 and $(NH_4)_2SO_4$] were applied, each at six rates, and all treatments were carried out in triplicate (108 pots in all).

The pots were waxed honey cartons holding 1044 g. of the silty fine sandy subsoil of a recent alluvial soil, which was purposely chosen for its low N content (0.0533 per cent). Basal dressings of 1 g. $CaCO_3$, 0.25 g. $Ca(H_2PO_4)_2$, 0.1 g. $MgSO_4$, 0.15 g. K_2SO_4, and 1 μg. Na_2MoO_4 were applied to each pot. The moisture content was maintained at approximately 70 per cent of the water-holding ca-

[1] The authors are indebted to the department of scientific and industrial research for a grant to cover the cost of this trial; also to the director of the Dominion Physical Laboratory for supplying the labeled nitrogen salts; and to Messrs. T. Rafter and G. Page for the numerous mass-spectrometric determinations. The figures were drawn by R. C. Blackmore, and in the conduct of the experiment considerable assistance was given by D. Bullen.

TABLE 1

Mean yields of dry matter of tops and roots of grass and clover per pot

Labeled N Applied per Pot	Grown Separately				Grown Together			
	Grass		Clover		Grass		Clover	
	Tops	Roots	Tops	Roots	Tops	Roots	Tops	Roots
mg	*g.*	*g.*	*g.*	*g.*	*g.*	*g.*	*g.*	*g.*
$(NH_4)_2SO_4$ treatments								
0	0.37	0.57	3.20	1.25	0.34	0.55	2.72	0.65
10.1	0.69	0.97	2.68	1.00	0.65	0.99	2.29	0.40
25.2*	1.41	1.98	2.72	1.03	1.49	1.32	1.98	0.52
49.6	2.32	1.99	3.30	1.03	2.05	2.07	1.90	0.71
99.2	4.55	4.20	2.97	1.05	4.64	2.69	1.59	0.53
198.4	9.26	4.50	3.75	1.22	9.33	3.51	0.79	0.40
Significant differences at 5% level	0.70	0.37	0.52	0.54	1.39	0.51	0.78	0.20
KNO_3 treatments								
0	0.37	0.45	3.17	1.07	0.22‡	0.59	2.31	0.71
9.9	0.69	0.83	2.95	0.95	0.60	1.11	1.80	0.51
24.7†	0.98	1.42	3.00	0.99	1.03‡	1.76	1.79	0.53
45.6	1.29	1.79	2.35‡	1.14	2.16	2.18	2.04	0.82
91.2	3.24	2.88	2.05‡	1.25	1.95‡	3.28	1.22	0.58
182.3	7.83	4.68	2.60‡	1.59	6.07	4.19	1.25	0.63
Significant differences at 5% level	1.14	0.77	—	0.24	—	0.61	1.02	0.28

* 24.8 mg. applied to grass alone.

† 22 8 mg. applied to grass alone.

‡ One or more replicates were overheated on drying and some charring resulted; little if any N appears to have been lost because the percentage N was higher in the overheated samples; yields of N for replicates, where one was overheated, were similar.

pacity by regular weighing and watering. To avoid leaching losses the pots were purposely not drained, but this occasionally caused air-locks and temporary waterlogging. Clovers were thinned to three plants per pot and grasses to four plants, both when grown separately and together. Nitrogen was applied in solution at the nominal rates of 0, 10, 25, 50, 100, and 200 mg. N per pot (for actual rates see table 1).

A preliminary trial showed that, at the two low rates of treatment, 10 atom per cent excess N15 was advisable for analytical purposes, and 5 atom per cent excess N15 adequate for the higher amounts. Since it was also shown that more than 50 mg. N applied all at once at the seedling stage seriously damaged the clovers, the 100- and 200-mg. rates were given in 50-mg. increments over a period of 10 days. The seeds were sown on January 29, 1954, and the nitrogen was applied after thinning on and after March 5. The pots were kept in the greenhouse

throughout and harvested on May 12, when the tops of the plants were cut off at soil level. The roots were separated by washing on sieves, and tops and roots were dried at 105°C. and weighed. Though a complete separation of grass and clover roots when grown together proved difficult, so far as could be seen no roots were left in the soil.

The tops and roots were analyzed for total N, and some of the soils were analyzed for NH_4 N, NO_3 N, and total N. After the normal titration of the excess acid in the Kjeldahl distillates, excess H_2SO_4 was added to the solutions, which, after suitable pretreatment, were analyzed by the mass spectrometer to determine the N15–N14 ratio.

RESULTS

Yields of dry matter

Yields of dry matter are given in table 1.

Grass grown separately. Less nitrogen was applied as KNO_3 than as $(NH_4)_2SO_4$, especially at the highest rates, but even after this was allowed, $(NH_4)_2SO_4$ gave slightly higher yields of dry matter than did KNO_3 (table 1). Lewis (10) in pot experiments and Walker, Adams, and Orchiston (18) in field experiments observed similar effects in a comparison of $(NH_4)_2SO_4$ with NH_4NO_3. Yields of tops (table 1) were related linearly to N applications for both forms of N within the limits of experimental error. Root yields lie on a smooth convex curve, the rate of increase falling off with higher levels of N. For the tops, the results support observations (19) that grasses will respond linearly to N over a very wide range of applications. The top–root ratio was rather less than unity at low levels of N, but gradually increased; for $(NH_4)_2SO_4$ it was just over 2 at the highest level.

Clover grown separately. Neither forms nor levels of N had much effect on the yield of clover tops or roots (table 1). In the early stages of growth clovers receiving mineral N showed a clear-cut benefit with increasing applications, but such differences largely disappeared by harvest. Caldwell and Richardson (4) observed similar results with alsike and red clover. There was evidence (scarcely significant but further substantiated by the data on N uptake) that for $(NH_4)_2SO_4$ at the time of harvest, yields were depressed at low levels of N but increased at the highest level. Root yields showed a similar trend. Thornton and Nicol (16) noted that mineral N may delay nodulation, but this will be of less consequence at high levels of N, because even if nodulation is delayed ample mineral N is available. Top–root ratios remained fairly constant at about 3:1.

Grass and clover grown together. It is well known that increasing levels of N change a condition of clover dominance into one of grass dominance. This is shown particularly well in the $(NH_4)_2SO_4$ series in table 1, where the yields of grass tops are almost identical with the yields of grass when grown alone, and clover yields greatly depressed. Root weights of the grass were rather less than when grown alone at the higher levels of $(NH_4)_2SO_4$, but with KNO_3 root weights were similar whether grass was grown alone or with clover. Root weights of clover were much lower when grown with grass than when grown alone, but within either

TABLE 2

Mean percentage N in tops and roots of grass and clover

Labeled N Applied per Pot	Grown Separately				Grown Together			
	Grass		Clover		Grass		Clover	
	Tops	Roots	Tops	Roots	Tops	Roots	Tops	Roots
mg.	%	%	%	%	%	%	%	%
$(NH_4)_2SO_4$ treatments								
0	0.90	0.67	3.12	2.61	0.80	1.53	3.53	2.76
10.1	0.80	0.64	3.15	2.50	0.81	1.15	3.03	2.63
25.2*	0.84	0.57	3.37	2.40	0.84	0.99	2.93	2.24
49.6	0.82	0.58	3.30	2.66	0.90	0.77	3.09	1.53
99.2	0.94	0.60	3.20	2.64	0.93	0.75	2.86	1.87
198.4	1.15	0.86	2.58	2.44	1.09	0.93	2.96	2.13
KNO_3 treatments								
0	0.74	0.68	3.52	2.68	1.29‡	1.25	3.42	2.57
9.9	0.75	0.64	2.96	2.53	0.87	0.93	3.40	2.35
24.7†	0.76	0.55	3.25	2.32	0.98‡	0.79	3.19‡	2.11
45.6	0.90	0.59	3.64‡	2.17	0.82	0.75	2.97	1.75
91.2	0.85	0.69	4.22‡	2.45	1.55‡	0.69	2.98	1.68
182.3	1.11	0.78	4.08‡	2.51	1.12	0.79	2.90‡	2.10

* 24.8 mg. applied to grass grown alone.
† 22.8 mg. applied to grass grown alone.
‡ At least one replicate scorched on drying—percentage N therefore high.

group they showed remarkably little variation. The difficulty of effecting a complete separation of grass and clover roots may have been responsible for the lower weights.

Percentage nitrogen in grass and clover

Replicates were usually bulked for determination of N (table 2). The percentage N in the grass was very low even at the highest N levels, and by harvest only traces of mineral N were present in any of the soils analyzed. Assuming that an acre of soil to a depth of 6–9 inches weighs 2×10^6 pounds, then the highest rate of about 200 mg. N per pot represents 400 pounds N per acre. As shown by Cooke and Millar (5), because of the favorable conditions for photosynthesis under greenhouse conditions, considerably heavier dressings than would be normal in the field may have to be applied to grow plants of comparable N status. The conditions of this trial clearly represent the lower part of the N-response curve. The percentage N in the grass tops was similar for forms of N whether grown alone or with clover. When grown alone, grass roots contained a somewhat lower percentage N than did the tops, but when grass was grown with clover the N content was occasionally higher in roots than in tops, perhaps because of a possible contamination of the grass roots with clover roots.

The N content in the clover tops was usually 3 or more per cent, and when

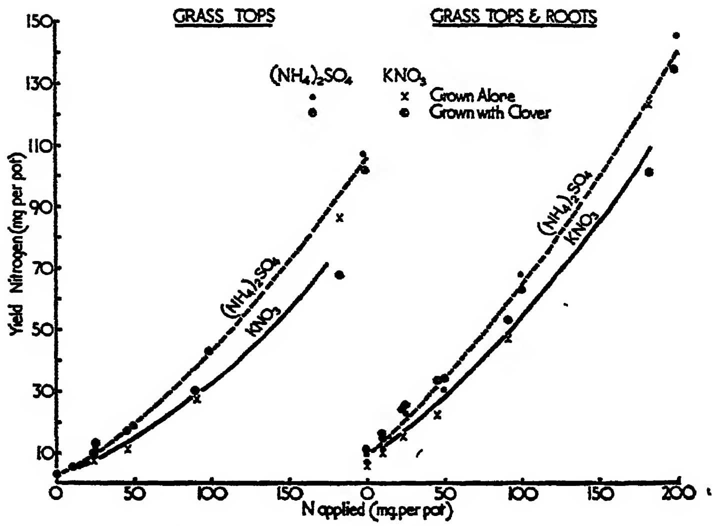

FIG. 1. RECOVERY OF N IN GRASS TOPS, AND IN TOPS PLUS ROOTS, GROWN ALONE AND WITH CLOVER

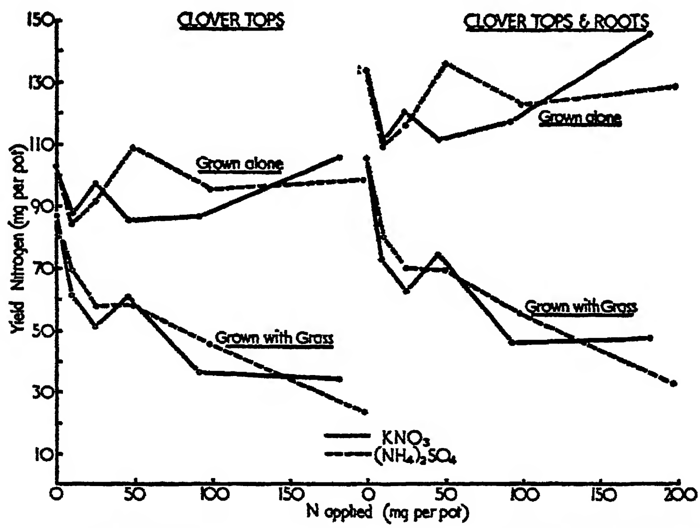

FIG. 2. YIELDS OF N IN CLOVER TOPS, AND IN TOPS PLUS ROOTS, GROWN ALONE AND WITH GRASS

grown with grass appears to have been depressed with increasing levels of N. As for grass grown alone the percentage N in the roots was appreciably lower than in the tops.

Nitrogen uptake per pot

Figures 1 and 2 show nitrogen uptake per pot for grass and clover respectively.
Grass. It is clear from figure 1 for both tops and tops plus roots that a slightly

lower recovery of N was obtained from KNO_3 than from $(NH_4)_2SO_4$. In absence of applied N, the soil supplied only about 3–4 mg. N to the tops and a total of 8–9 mg. for tops plus roots. Yields of N in the grass were very similar whether the grass was grown alone or with clover, and even without consideration of the N15 data, and even under conditions of clover dominance, it can be assumed that grasses have taken up all the mineral N available when grown with clovers. Apparently little if any N was transferred underground from clover to grass during the 15 weeks of the experiment. The curves are slightly more concave for tops than for tops plus roots as a consequence of the lower top–root ratios at the low N levels, and the percentage recovery of N in the tops gradually increased to nearly 50 per cent for the highest N levels. For tops plus roots, recovery approached 65 to 70 per cent at the highest levels. If a more fertile soil had been used, one which supplied N equivalent to the 100-mg. level, some 65 per cent of the first 100 mg. N applied as $(NH_4)_2SO_4$ might have been recovered in the tops, and about 75 to 80 per cent in the tops plus roots.

Clover. As for dry matter, clover grown alone yielded about as much N in both tops and roots whether given combined N or not (fig. 2). Yields of N may have been reduced with small amounts of combined N, in agreement with the results of Thornton and Nicol (16) working with lucerne in sand culture. The yield of N in the clover was depressed when this crop was grown with grass, and the lower levels of combined N had a relatively greater effect than the higher levels, confirming previous observations in the field (18).

Yield of N in tops of grass plus clover when grown together. This yield of N (fig. 3) is of considerable significance in practice, since nitrogen is widely applied to grass-clover associations with varied results, although much depends on subse-

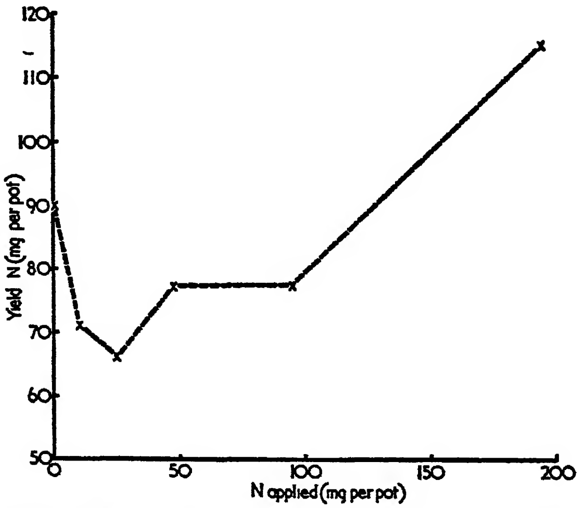

FIG. 3. EFFECT OF N LEVELS ON TOTAL YIELD OF N IN TOPS OF GRASS AND CLOVER WHEN GROWN TOGETHER

Both forms of N averaged

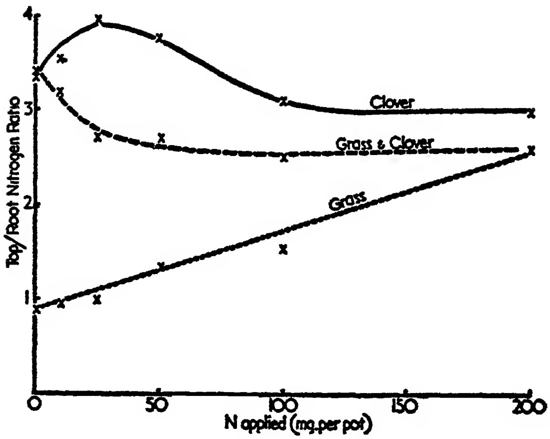

FIG. 4. EFFECT OF N LEVELS ON TOP-ROOT NITROGEN RATIOS
Both forms of N averaged

quent management. From figure 3 it is clear that, because of the marked suppression of clover at the lower N levels, the total yield of N fell, despite the almost linear response of the grass to applied N. The total yield eventually increased at the highest N level, partly because of the reduced degree of suppression of clovers. Remy and Vasters (13) quoted by Thornton and Nicol (15) found exactly the same effect in pot trials, and we have had similar results in the field (18). In practice, this means that light applications of combined N to a clover-dominant sward may give a lower yield of N than if no fertilizer were used, which is in marked contrast to the effect on a grass-dominant sward.

Top–root nitrogen ratios

The averages for the two forms of combined N are shown in figure 4. For grass grown alone the ratio rose from about 1 to 2.5, and for clover grown alone the ratio rose initially from about 3.5 to 4 and then declined to 3. We have examined the results of several trials (19) in which about 65 per cent of the N applied to grasses over a wide range of applications was recovered in the tops, and it was suggested that nitrogen applied to grasses would be distributed approximately in a 2–1 ratio between tops and roots. Obviously this can be only an average ratio with many factors causing deviation from it. At very low levels of N nutrition our data show clearly that the top–root ratio is nearly 1, and that it increases at higher N rates. This may account in part for the lower part of the S-shaped response curves on soils seriously deficient in a given nutrient, for a more nearly linear response is obtained from tops plus roots. Stage of growth is probably another factor, for until the cotyledons have emerged a germinating seedling will have a top–root ratio of zero. The highest level of N gave a top–root ratio of about 2.5, but the pots were packed tight with roots, which emerged on the surface; root growth might have been more extensive in a larger volume of soil.

TABLE 3

Total yields of N and labeled N in tops plus roots per pot

Labeled N Applied per Pot	Grass Grown Alone		Clover Grown Alone		Grass and Clover Grown Together			
					Grass		Clover	
	Total N	Labeled N	Total N	Labeled N	Total N	Labeled N	Total N	Labeled N
mg.	*mg.*	*mg.*	*mg.*	*mg.*	*mg.*	*mg.*	*mg.*	*mg.*
$(NH_4)_2SO_4$ treatments								
0	7.2	0	132	0	11.0	0	114	0
10.1	11.7	3.7	109	0.5	16.5	3.7	80	0.1
25.2*	23.1	12.5	116	1.8	25.6	9.4	70	0.6
49.6	30.4	20.2	136	3.6	34.3	20.3	70	2.7
99.2	67.9	51.4	123	23.5	63.1	46.1	55	3.8
198.4	145.6	123.1	129	85.5	135.0	108.2	32	6.2
KNO_3 treatments								
0	5.8	0	135	0	10.2	0	97	0
9.9	10.5	3.9	111	1.1	15.5	3.7	73	0.4
24.7†	15.1	8.4	121	3.1	24.2	9.3	63	0.9
45.6	22.2	14.3	110	6.7	33.8	21.0	75	3.3
91.2	47.4	36.1	117	16.6	52.9	35.0	46	3.9
182.3	123.2	108.2	145	57.7	100.6	82.1	47	8.4

* 24.8 mg. applied to grass grown alone.

† 22.8 mg. applied to grass grown alone.

N15 data

The total yields of N and labeled N are presented in table 3.

Uptake of labeled N by grass grown alone. At the end of the experiment, only traces of mineral N were found in any of the soils; all the labeled N must have been utilized by the plants or soil organisms and, in the latter case, converted into organic N or lost by denitrification. In absence of applied N, the soil supplied an average of 6.5 mg. of normal N to the grass grown alone. At the highest N rates the normal N contents were 22.5 and 15.0 mg. for $(NH_4)_2SO_4$ and KNO_3, respectively, the amount of normal N increasing with N levels. This implies that the grass took up increased amounts of mineralized soil organic N of normal N15–N14 ratio, and thus confirms the data of other workers who suggest there is a continual cycle of mineralization and immobilization of N by soil organisms, the labeled mineral N being removed by organisms and replaced by normal mineral N. The situation may be further complicated if plants absorb N14 preferentially, but our data throw no light on this problem.

Uptake of labeled N by clover grown alone. For both forms of N at all levels (table 3), clovers took up much less labeled N than did grass. Clearly, clover took up more labeled N as more was applied and fixed correspondingly less symbiotically, a point already established by Thornton (14) for soybeans and on *a priori* grounds by many other workers using normal mineral N.

Uptake of labeled N by grass and clover grown together. For all but the highest levels of N, grass grown with clover apparently gave slightly higher yields of total N than when grown alone (table 3), but it is doubtful whether this difference is significant, particularly as at low N levels clovers were dominant and clover roots may have contaminated the grass roots. At the highest levels of N (both forms), yields of total and labeled N were lower than when the grasses were grown alone. Some of the grass roots may have been weighed as clover roots (grasses were dominant at these high N levels), but even if all the labeled N harvested in the tops and roots of the clovers is included with the grass N, the total yield of labeled N is still less than the yield of labeled N in the grasses grown alone. This may be due to experimental error or a higher rate of microbial replacement of labeled N by normal mineral N.

Clover grown with grass obviously took up only a small fraction of the labeled N (both forms) at all levels. With the suppression of clovers due to increased yields of grass as N was applied, however, the labeled N became a larger fraction of the total N contained in the clovers—from less than 1 per cent at low levels of N to about 20 per cent at the highest level. If the total amounts of labeled N taken up by the grass and clover are compared with the labeled N taken up by the grass grown alone, they are lower but approximately of the same order, especially in the case of $(NH_4)_2SO_4$.

Labeled N in soil and final balance sheets. Assuming homogeneity, the soil in each pot at the beginning of the experiment should have contained 556 mg. N. At the end of the experiment only traces of mineral N were found in the soils even in the pots growing clovers alone, which had received about 200 mg. of labeled N, of which only some 60 or 80 mg. was recovered in the clovers. Only selected soils were analyzed for total N and labeled N, and significant amounts of labeled N in the organic form were present in all soils that had been treated wth labeled N; in the soils growing clovers alone, the percentage N in the soils was probably significantly higher than at the beginning, for example, for the $(NH_4)_2$-SO_4 treatments the amounts of N per pot were 579, 629, and 648 mg. for the 0-, 99.2-, and 198.4-mg. treatments, respectively. Smaller increases or even occasionally lower contents were found in grass alone or in grass plus clover pots, but the determination of total N in the soils, with all the consequent sampling and analytical errors, precludes any precise observations. The amounts of labeled N present in the soils from the two highest N levels, all but a minute fraction in the organic form, are shown in table 4.

The soil data show clearly that although clover grown alone took up less labeled N than did grass or grass plus clover, considerably more labeled N remained in these soils. In their sand culture experiments Trumble and Shapter (17) noted an accumulation of N where clover was grown alone but attributed it to root residues. A small amount of clover roots may have been included in the soil in the experiments reported here, but even so, this would certainly not account for all the labeled N found in the soil, which in almost all cases exceeded the total uptake of labeled N by the clovers.

It is most striking that no matter what plants were grown in the pots, the

TABLE 4

Recovery of labeled N in plants (tops plus roots) and soil

Mg	$(NH_4)_2SO_4$ Treatments						KNO_3 Treatments					
	99.2 mg. labeled N			198.4 mg. labeled N			91.2 mg. labeled			182.3 mg. labeled N		
	G*	C*	G+C*	G	C	G+C	G	C	G+C	G	C	G+C
Recovery in												
Grass........................mg./pot	51	—	46	123	—	108	36	—	35	108	—	82
Clover........................mg./pot	—	24	4	—	86	6	—	17	4	—	58	8
Soil........................mg./pot	16	39	27	27	59	34	25	43	19	29	78	27
Total recovery..................mg./pot	67	63	77	150	145	148	61	60	58	137	136	117
Mean recovery amount.........mg./pot	69			148			60			130		
Percentage of total applied............	70			75			66			71		

* G = grass grown alone; C = clover grown alone; and G + C = grass and clover grown together.

total recovery of labeled N was similar (with one or two exceptions) for the same rates of applied N, with a slightly higher percentage recovery from $(NH_4)_2SO_4$ than from KNO_3 (table 4). In view of the numerous sources for possible error, these recoveries are remarkably uniform. Although it is not possible to check the statistical significance of these slight differences, and therefore the recovery at different rates of N (both forms), the percentage recovery probably was slightly higher at the higher rates, although the absolute losses of labeled N were also higher (about 30 mg. and 50 mg. per pot at the lower and higher rates, respectively).

DISCUSSION

These experiments have demonstrated clearly that, when grass and clover are grown together, the grass utilizes almost all the mineral N made available from the soil or applied in the fertilizer form, for in a wide range of applications only about 5 to 6 per cent of the applied N was recovered in the clover. The situation is quite different when clovers are grown alone, for then the clovers will absorb appreciable amounts of mineral N but fix correspondingly less N symbiotically; much of the unabsorbed mineral N accumulates in the organic form in the soil.

In respect to the top–root ratios of the utilized N discussed earlier, Pinck and Allison (12) obtained similar data with Sudan grass in pots, the top–root ratio widening with increasing rates of N from about 1 to 2 for mature plants. This situation may not be exactly comparable with the effects on established grass plants in the field, and it cannot be argued that the top–root ratio of 3 to 4 observed for the clover would necessarily hold under field conditions for established plants.

Pinck and Allison (12) could not account for about a third of the applied N,

and in these experiments the amount of N lost almost certainly by denitrification could be represented by a similar fraction. MacVicar *et al.* (11), Broadbent and Stojanovic (3), Jones (8), and others working with inorganic sources of N15, and Arnold (1), making direct determinations of N_2O, have all shown that denitrification even under relatively well-aerated conditions, is probably a more important factor than was supposed, and is still more pronounced under conditions of poor aeration. Our pots were not well aerated, and some losses could therefore be expected. Losses of N by denitrification appear to be less with NH_4-N than with NO_3-N (3, 8). Although in the present trials NH_4-N may have been rapidly nitrified, losses from NO_3-N appear to have exceeded slightly the losses from NH_4-N. Denitrification losses have been shown to be great in soils that are low in organic matter (2, 11) and of neutral to alkaline pH (2). Since this soil contained 0.48 per cent carbon and had a pH of 6.6, conditions would seem to have been favorable for denitrification on several counts.

Hiltbold *et al.* (7) showed that large amounts of mineral N were immobilized in soil organic matter, a point further demonstrated by Wallace and Smith (21), whether or not organic matter was added to the soil. This effect, as observed in our trials, is almost certainly due to the dynamic microbial cycle, an explanation given theoretical consideration by Kirkham and Bartholomew (9). Where clover was grown alone, more labeled N accumulated in the organic form in the soil than where grass was grown alone. This could be due to a greater exchange of labeled N for soil N, but, as the total soil N increased markedly, a more likely explanation is that soil organisms (possibly rhizosphere organisms) utilized both labeled N and energy material obtained from or excreted by the clover roots. Where grass was grown alone, the data indicate that exchange of labeled N for soil N increased with increasing levels of labeled N. This may be because the developing grass took longer to absorb the greater amounts of N and there was, consequently, a longer period over which exchange could take place. Percentage losses by denitrification were similar, but probably slightly less at the 200-mg. rate compared with the 100-mg. rate, and support Arnold's observation (1) that losses are related linearly to applications.

These losses of 30 per cent of the applied N do not support our conclusions (19) that almost all the fertilizer N applied to pastures is recovered by the grasses in the approximate ratio of 2 to 1 for tops to roots, but the conditions are not directly comparable. First, the experimental conditions favored denitrification. Second, the grasses were in the seedling stage when the labeled N was applied, and the undeveloped root systems may not have been able to compete so intensively with microorganisms for mineral N as would the more massive root system of established plants. It is noteworthy that only a slight increase in yield of root N occurred between the 100- and 200-mg. treatments (perhaps because of potbound conditions already reached at the 100-mg. level), and about 63 mg. of N was recovered in the grass tops from the extra 100 mg. of the highest treatment. If, in the field, maximum or near maximum root development had already occurred before fertilizer N was applied, then recoveries of two thirds of the N in the grass tops could mean that a third of the fertilizer N was lost by denitrifica-

tion or leaching. There is little doubt, however, that in established pastures old roots are continually decomposing and being replaced by new roots, and certainly for grasses, where the C–N ratio of the roots may be fairly high, mineral N is needed not only for the formation of new roots but also by microorganisms during the decomposition of old roots. It is difficult to imagine under these conditions that losses by denitrification could be as high as 30 per cent. Furthermore, if, as in New Zealand, no fertilizer N is usually applied to pastures, there is (except in urine patches) very little accumulation of mineral N and possibly little opportunity for denitrification to take place. There will normally be intense competition for mineral N by growing grasses and microorganisms decomposing old roots, and consequently, the activity of denitrifying organisms may be severely restricted.

There still remains the possibility that a considerable amount of N may be lost by denitrification under conditions of poor aeration (poaching by stock and poor drainage) and under the unique conditions of the urine patch, where some 400 pounds N per acre may be returned and large amounts of mineral N may accumulate at least temporarily (6). These losses were possibly underestimated by us in a theoretical treatment of the N cycle in grassland soils (19), but we were only trying to establish general principles, the details of which can be modified as our knowledge increases. Indeed, if we modify our data in light of some of the observations made in this trial, the calculated equilibrium level of soil nitrogen in the best New Zealand pastures is nearer 1 per cent than the original calculated level of 1.8 per cent; this figure of 1 per cent is much nearer the observed values on the older high-producing pasture soils.

No evidence of underground transference from clovers to grasses was observed during the course of this trial. Field experiments (19) have shown beyond any question, however, that such transference does occur, whether by direct excretion or by decomposition of clover roots and nodules, and although much is known about the conditions under which such transference occurs (22), the subject clearly merits further attention.

SUMMARY

$(NH_4)_2SO_4$ and KNO_3 labeled with N15 were applied at various levels to grass and clover grown separately and together. The distribution of this N in tops, roots, and soil was studied.

Regardless of the plants grown, approximately 30 per cent of the labeled N was lost, presumably by denitrification, under the particular conditions of these trials. Slightly higher losses were noted from KNO_3 than from $(NH_4)_2SO_4$. In all cases some labeled N was converted into soil organic N, and where clover was grown alone, rather more was recovered from the soil than in the clovers.

Clover grown alone utilized considerably less labeled N than did grass grown alone, and with increasing levels of combined N, more N was taken up and correspondingly less fixed symbiotically.

When grass and clover were grown together, the grass contained about 95 per cent of the utilized N at all rates of application, and there was little difference be-

tween uptake of N by grass whether grown alone or with clover. There was no evidence of any significant underground transference of N from clover to grass.

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COPPER AND ZINC EXCHANGE FROM DILUTE NEUTRAL SOLUTIONS BY SOIL COLLOIDAL ELECTROLYTES

L. E. DEMUMBRUM AND M. L. JACKSON

University of Wisconsin[1]

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This study was undertaken to determine the extent to which two neutral colloidal electrolytes, Ca montmorillonite and Ca peat, were operative in accumulating Cu and Zn ions from slightly soluble salts or oxides of these cations. Any appreciable accumulation of these ions in exchangeable form from very dilute neutral solution might explain, in part, the ability of plants to obtain Cu and Zn from neutral or slightly alkaline soils in sufficient quantities to support normal growth. In a number of systems a solution of 0.5 N $Ca(OAc)_2$ was employed as a suspension medium to prevent any pH gradient across the systems. At the same time, the sorption of Cu and Zn in presence of a large excess of Ca ion was noted.

A number of investigators have studied the effect of soil colloidal electrolytes on the weathering of soil-forming minerals and related compounds. Bradfield (1) showed that slightly soluble salts, such as $Ca(OAc)_2$ and $BaSO_4$, were made more soluble by presence of Na montmorillonite. Electrodialized montmorillonite was used by Graham (7) to effect the decomposition of six soil-forming minerals. This phenomenon was demonstrated again by McClelland (8). Gibbs and Marshall (6) used acid montmorillonite to decompose in part several copper-bearing minerals.

MATERIALS

One-gram samples of CO_3-free California montmorillonite (representing the montmorillonite series of minerals) were washed three times with N neutral $Ca(OAc)_2$ and several times with ethanol to remove excess salt. The exchange capacity of the montmorillonite had been previously determined by use of N neutral $Ca(OAc)_2$ to be 110 me. per 100 g.

One-gram samples of Carlisle peat (66.1 per cent organic matter, with the inorganic fraction composed of quartz, feldspar, and mica) were ground to pass a 40-mesh sieve and leached with N neutral $Ca(OAc)_2$ and with ethanol to remove excess salt. The exchange capacity was determined by use of N neutral $Ca(OAc)_2$ to be 150 me. per 100 g.

Several chemical precipitates were prepared and used in the experiment: $Cu(OH)_2$ was prepared by adding dilute KOH to $CuSO_4$ and washing the precipitate several times with ethanol to remove excess bases and salt; $Cu_3(PO_4)_2$ was prepared by adding NaH_2PO_4 to an excess of acidified $CuSO_4$ and washing the precipitate several times with ethanol to remove excess salts; $Zn(OH)_2$ was pre-

[1] The work described in this paper was presented before the North Central Branch of the American Society of Agronomy, Ames, Iowa, June 29, 1955, and was supported in part by the University of Wisconsin Research Committee through a grant of funds from the Wisconsin Alumni Research Foundation.

pared in the same manner as $Cu(OH)_2$, and $Zn_3(PO_4)_2$ in the same manner as the $Cu_3(PO_4)_2$. Reagent grade CuO was employed.

METHOD

As cation sources, 0.5-g. samples of slightly soluble salts or oxides, including $Cu(OH)_2$, CuO, $Cu_3(PO_4)_2$, $Zn(OH)_2$, and $Zn_3(PO_4)_2$, were placed in separate Cellophane dialysis bags. As colloidal electrolytes, 1-g. samples of Ca montmorillonite or Ca peat, prepared by washing first with a *N* neutral $Ca(OAc)_2$ solution and then with 95 per cent ethanol to remove excess salt, were placed in other dialysis bags. One colloidal electrolyte material and one cation source were placed in each container. For room temperature equilibrium, a 60-ml. Pyrex bottle was used, and for the steam plate equilibrium a 600-ml. beaker. The containers were filled with either CO_2-free distilled water or 0.5 *N* $Ca(OAc)_2$. Different systems were equilibrated 2.5 to 3.5 months at room temperature, or 2 to 3 weeks on the steam plate. In one instance a $Cu_3(PO_4)_2$ leachate was used as the suspension medium and Cu source. At the end of the prescribed period the colloidal electrolyte material was removed, washed with ethanol, and extracted with acid NH_4OAc. This extract was analyzed for Cu or Zn. In the systems to which had been added an excess of $Ca(OAc)_2$, the extract was analyzed for exchangeable Ca as well.

In addition to the previous measurements, the usual Ca, Cu, and Zn exchange capacities were determined by washing the colloid four times with the appropriate acetate salt solution and five times with ethanol, followed by extraction with acid NH_4OAc, and analysis of the extract for the cation in question. Ca was determined on the Beckman model Du flame spectrophotometer; Cu by a carbamate method (2); and Zn by a dithizone method (3).

RESULTS

Cu and Zn exchange in neutral systems

Considerable quantities of Cu and Zn were exchanged on the colloidal electrolyte materials from dilute neutral solutions (table 1). The amount exchanged increased when the exchange reaction was carried out at an elevated temperature (table 1). From 0.7 to 3.4 per cent of the montmorillonite exchange capacity as determined by $Ca(OAc)_2$ (table 2) became saturated with Cu, and 6.1 to 27.2 per cent of the peat exchange capacity became thus saturated. The exchange of Zn from $Zn_3(PO_4)_2$ was appreciable in the montmorillonite and extensive in the peat. The more soluble $Zn(OH)_2$ supplied large quantities of Zn in exchangeable form to both colloidal electrolytes. Concentrations of Cu and Zn per unit weight of clay were 500 to 20,000 times greater than concentrations per unit weight of solution.

The room-temperature systems were rather sensitive to the amount of Cu or Zn supported in solution by the precipitate used. For instance, more Cu was sorbed from $Cu(OH)_2$ than from CuO, and sorption of Zn from $Zn(OH)_2$ was appreciably faster than from $Zn_3(PO_4)_2$. This discrepancy was much less noticeable in the steam plate experiments, in which more nearly equal amounts of Cu

TABLE 1

Sorption of Cu and Zn by montmorillonite and peat from very dilute neutral solutions

Colloidal Electrolyte	Treatment*	Sorption: Room temperature	Sorption: Steam plate
		me./100 g.	me./100 g.
		65 days	14 days†
Ca montmorillonite	CuO	0.8	2.9
	$Cu(OH)_2$	2.7	3.7
	Blank	0.0	0.0
Ca peat	CuO	9.2	41.0
	$Cu(OH)_2$	15.4	41.1
	Blank	1.3	0.4
		98 days	21 days
Ca montmorillonite	$Zn(OH)_2$	74.5	—
	$Zn_3(PO_4)_2$	0.7	—
	Blank	0.0	—
Ca peat	$Zn(OH)_2$	—	83.0
	$Zn_3(PO_4)_2$	—	78.0
	Blank	—	0.5

* Equilibrium pH values were all within the range of 6.9 to 7.1.

† Followed by 7 days at room temperature.

or Zn were sorbed, regardless of cation source. This indicates that equilibrium was more nearly attained in the steam-plate systems.

Epstein and Stout (5) data indicate that the quantities of Cu and Zn exchange saturation obtained in the present experiments, even at pH 7, would be highly significant in relation to plant nutrition. The exchange of appreciable quantities of Cu and Zn from the insoluble materials may explain, in part, the ability of plants to obtain sufficient Cu and Zn from neutral or slightly alkaline soils. Also, it may explain why a variety of compounds, regardless of their solubilities in water, are effective sources of Cu and Zn for plants.

Effect of $Ca(OAc)_2$ buffer

In presence of excess $Ca(OAc)_2$, Ca occupied 110 me. per 100 g. of the montmorillonite exchange (table 2). This equaled the exchange capacity as measured by N neutral $Ca(OAc)_2$. In addition to Ca, considerable quantities of Cu or Zn were sorbed in presence of the large excess of soluble Ca ions. The excess equaled 10 me. per 100 g. for Cu and 4 me. per 100 g. for Zn, or about 10 per cent and 4 per cent, respectively, of the Ca exchange capacity. The combined exchangeable Ca plus Cu of montmorillonite in this case, and also that exchanged from an acid 0.5 N $CaCl_2$–0.1 N $Cu(OAc)_2$ system, were about equal to the exchange capacity measured by $Cu(OAc)_2$ in acid solution (table 2). Similarly, the combined Ca plus Zn exchange capacity was equal to that measured by $Zn(OAc)_2$. Evidently

TABLE 2

Sorption of Ca, Cu, and Zn by Ca montmorillonite

Treatment	Equilibrium pH	Exchangeable Cations			
		Ca	Cu	Zn	Total
		me./100 g.	*me./100 g.*	*me./100 g.*	*me./100 g.*
$Ca(OAc)_2$*..........................	7	110	—	—	110
$Cu(OAc)_2$*..........................	4	—	122	—	122
$Zn(OAc)_2$*..........................	6	—	—	114	114
$CaCl_2 + Cu(OAc)_2$.................	4	58	66	—	124
Ca montmorillonite, Ca $(OAc)_2$ with $Cu_3(PO_4)_2$ as Cu source, on steam plate............................	7	110	10	—	120
Ca montmorillonite, $Ca(OAc)_2$ with $Zn_3(PO_4)_2$ as Zn source, on steam plate............................	7	110	—	4	114

* Exchange capacity, as determined in the usual manner.

sorption of Cu or Zn can take place in excess of the Ca exchange saturation and the amount of excess is a function of the cation species used. In both acid and neutral solutions part of the montmorillonite exchange measured by Cu or Zn was not measured by Ca. This phenomenon demonstrates that, from pH 4 to pH 7, part of the exchange is specific for Cu or Zn. Corroborative studies, including infrared absorption evidence on the exchange mechanism in montmorillonite and peat, are presented separately (4).

A similar phenomenon was noted when Carlisle peat was used as the exchange material. Ca-saturated peat, in presence of 0.5 N $Ca(OAc)_2$, was shown to sorb Cu from very dilute neutral solution (table 3). The Ca present on the peat exchange was found to be about equal to or slightly greater than the Ca exchange capacity as measured by N neutral $Ca(OAc)_2$. In addition to the 155 me. per 100 g. of Ca present on the peat exchange, 14 to 22 me. of Cu was found to be sorbed from the $Cu_3(PO_4)_2$ source. This amount was in excess of the Ca exchange capac-

TABLE 3

Sorption of Ca and Cu by Ca peat

Treatment	Equilibrium pH	Exchangeable Cations		
		Ca	Cu	Total
		me./100 g.	*me./100 g.*	*me./100 g.*
$Ca(OAc)_2$*..........................	7	150	—	150
$Cu(OAc)_2$*..........................	4	—	180	180
Ca peat, $Ca(OAc)_2$ with a $Cu_3(PO_4)_2$ leachate as Cu source, on steam plate............................	7	155	14	169
Ca peat, with a $Cu_3(PO_4)_2$ leachate as Cu source, on steam plate..........	7	155	22	177

* Exchange capacity, as determined in the usual manner.

ity, and the combined Ca plus Cu on the exchange approached the exchange capacity of the peat as measured by $Cu(OAc)_2$ in acid solution. This suggests that part of the peat exchange is specific for Cu in acid and neutral solutions.

SUMMARY

A special technique was developed by which the exchange of Cu or Zn from relatively insoluble compounds to colloidal electrolytes could be examined. Slightly soluble salts or oxides of Cu or Zn were placed in separate dialysis bags. Other bags were filled with Ca montmorillonite or Ca peat. One bag containing a colloidal electrolyte material and a second containing a cation source were placed in a container filled with CO_2-free distilled water. Time was allowed for exchange to take place either at room temperature or on the steam plate. In a number of the systems, 0.5 N $Ca(OAc)_2$ solution was used as the suspension medium.

Results may be summarized as follows:

Ca montmorillonite and Ca peat accumulated considerable quantities of exchangeable Cu or Zn from the very dilute neutral solution supported by a relatively insoluble salt, oxide, or hydroxide of these cations. This phenomenon occurred in presence or absence of excess Ca ions.

Peat and montmorillonite seemingly have an increment of exchange capacity that is specific for cations such as Cu and Zn in acid and neutral solution.

It is proposed that the ability of soil colloidal electrolyte materials to accumulate exchangeable Cu and Zn from extremely dilute neutral solution is significant from the standpoint of plant nutrition.

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A SLOWLY SOLUBLE SOURCE OF MICRONUTRIENTS FOR PLANTS

W. A. RHOADS, A. WALLACE, AND E. M. ROMNEY

University of California, Los Angeles[1]

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Slowly soluble fertilizer compounds are of considerable interest as a means of maintaining an available source of nutrients to plants over a long period and also as a means of preventing toxicity. Since a successful product would be extremely valuable, efforts to produce one are commendable. Maintenance of an available supply of iron in certain soils and also occasionally in solution and sand cultures is difficult. Use of a relatively insoluble iron source in culture work dates back to 1849 and the work of Salm-Horstmar (8). In recent years a number of workers have investigated the use of somewhat similar sources of iron and other micronutrients (1, 2, 7, 9, 11, 14–18), and some of their studies led to the development of a series of insoluble "glassy frits" that have been investigated for possible agricultural use (11, 14–18). The present study evaluates some of these glassy products as a means of supplying a slowly available source of iron and other micronutrients to plants.

MATERIALS AND METHODS

Experiment 1

Bean plants, variety Six-Weeks-Bush, were germinated and planted in 5-inch clay pots containing a naturally calcareous soil of the Yolo series. This soil contained 3 per cent $CaCO_3$. FTE products,[2] numbers 233-A, 253-A, and 266, had been incorporated into the soil at rates equivalent to 0; 1000; 4000; 30,000; and 100,000 pounds per acre 6 inches. Micronutrient content and solubilities of these materials are given in table 1. Three bean plants were planted in each pot, and three pots were included in each treatment. Plants were grown for 4 weeks, then harvested, acid-washed with 0.3 N HCl, dried at 70° C., and ground for analysis. Leaves and stems were combined for the micronutrient determinations and roots were discarded.

Experiment 2

A 5-pound quantity of the mixture of proper silicate materials and micronutrients, except iron, was obtained from the manufacturer of FTE materials, whose number for this particular mixture was 628. To a quantity of this mixture, sufficient Fe_3O_4 that had been tagged with Fe59 was added, so that the final FTE product was tagged with 100,000 counts per minute per milligram of Fe as determined with a Nuclear-Chicago scintillation well counter. This mixture was fused

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[2] Products of Ferro Corporation. FTE is the trade name for this series of products and stands for "fritted trace elements."

TABLE 1

Solubility in different reagents of Fe, Mn, Zn, and B from three different FTE products

Number of FTE* Product	Micronutrients Leached from 1 G. FTE with 10-ml. Solution				Total Fe leached from FTE
	Fe	Mn	Zn	B	
	ppm.	*ppm.*	*ppm.*	*ppm.*	%
Leached with pH 5 NH_4 acetate					
266	1140	7	426	17	4.5
233A	3390	15	29	69	1.2
253A	440	22	196	33	0.3
Leached with pH 7 NH_4 acetate					
266	2	1	—	21	0.008
233A	3	11	—	72	0.001
253A	2	1	—	28	0.001
Leached with pH 7 NH_4 acetate plus a chelating agent					
266	230	3	246	16	0.9
233A	440	4	13	77	0.2
253A	180	15	131	29	0.1
Leached with a chelating agent at pH 7					
266	270	4	291	5	1.1
233A	390	11	6	61	0.1
253A	180	10	30	15	0.1

* According to the commercial reports, FTE 233A contained 28% Fe; 253A contained 12.3% Fe, 6.0% Mn, and 4.0% Zn; and 266 contained 2.5% Fe and 18.1% Zn. Each was made from borosilicates and, hence, contained B.

at 1260° C., which was reached in 7 hours and held for 2 hours, then quenched and ball-milled in a glass jar with quartz balls until the following size distribution was obtained on Rotap dry sieves:

>20 screen	0.0%
<20–>60	0.0%
<60–>100	5.0%
<100–>150	14.7%
<150–>200	16.5%
<200–>325	26.8%
<325	37.0%

This particle-size distribution was essentially the same as that of materials produced commercially.

This product, which contained 4.19 per cent Fe, was applied to soils in glasshouse pot tests. The weighed quantity for each pot was thoroughly mixed into the soil by the use of a McClelland Batch Mixer, which mechanically rotated the sample at 6 rpm. for 25 minutes. The FTE was mixed in the soil at rates equiva-

TABLE 2

Some properties of Sassafras, Hanford, and Sorrento soils used in Experiment 2

Properties	Sassafras	Hanford	Sorrento
Soil pH	4.6	6.6	8.0
$CaCO_3$ ... %	0.0	0.0	1.5
Cation-exchange capacity ... *me./100g.*	6.0	8.2	15.1
Exchangeable cations			
Potassium ... *me./100g.*	0.01	0.37	0.62
Calcium ... *me./100g.*	0.4	4.5	12.4*
Magnesium ... *me./100g.*	0.02	0.26	1.13
Sodium ... *me./100g.*	0.02	0.14	0.91
Texture	Sandy loam	Sandy loam	Fine sandy loam
Sand ... %	76.0	72.0	45.0
Silt ... %	14.0	20.0	42.0
Clay ... %	5.0	5.0	13.0
Soil organic matter ... %	1.58	1.45	1.52
Predominant clay	Kaolinite	Illite	Kaolinite and montmorillonite

* Calculated by subtraction of K, Mg, and Na from total cation-exchange capacity.

lent to 0; 50; 200; 1000; 5000; and 15,000 pounds per acre 2 million pounds. The commercial recommended rate is 25 to 50 pounds per acre. Three different soils were used: Sassafras sandy loam, an acid soil; Hanford sandy loam, an almost neutral soil; and Sorrento fine sandy loam, an alkaline calcareous soil. Other characteristics of these soils are given in table 2. One Eureka lemon cutting, 20 barley plants, and three soybean plants were grown in each soil for each level of FTE. Each treatment was replicated three times.

Because of smog[3] injury (6), the barley crop was grown only from November 18 to December 5, 1954, when the foliage of the crop was removed and an additional crop of barley planted in the same pots. This crop was allowed to grow from December 18, 1954, to January 28, 1955; the soybean crop was grown from December 8, 1954, to January 28, 1955; and the Eureka lemon cuttings grew from November 18, 1954, to February 11, 1955. These plants were also acid-washed, dried, and ground. Weighed portions of the ground plant materials were counted for Fe59 in the scintillation well counter. Materials were then analyzed for total Fe, Mn (12), and B (4). The amounts of Fe supplied to the plants by the tagged FTE product were calculated as parts per million of Fe from specific activity relationships between Fe59 and nonradioactive Fe.

After the crops had been grown, some extraction studies were made of the soils receiving the 15,000 pounds of FTE per acre. Five-gram samples of soil were vigorously shaken for 6 hours and then allowed to stand another 12 hours in presence of 10 ml. of *N* Na acetate that contained 0.1 per cent Na salt of a chelating agent commercially known as Chel 138. Determinations for radioactive Fe and also for total Fe were made on the extracts.

[3] Smog is, at least in part, ozone-oxidized unsaturated hydrocarbons in the atmosphere. In the Los Angeles area air pollution is referred to as smog.

RESULTS AND DISCUSSION

Experiment 1

The yields and Fe, Mn, and Zn contents of the Six-Weeks-Bush beans are given in table 3. Though the application rates were high, they failed to increase growth, but possibly no deficiencies existed in the soil. The highest rate of application decreased yields, apparently as a result of toxicity. The contents of Fe, Mn, and Zn indicate that no one of these elements was the cause of the toxicity. There was some evidence in the data that FTE 233-A, a high-Fe product, increased the Fe contents of the beans, especially at the rates of 1000 and 4000 pounds per acre. FTE 266, a high-Zn product, did not increase Zn contents for the rate of 1000 pounds per acre, but appeared to have a slight influence at the higher rates.

The results of Experiment 1 can be further clarified. The Na content of FTE products may be of considerable importance at very high application rates. There are indications that the Na can be hydrolyzed and, at least at high application rates, can increase the pH of the soil. In a separate study involving avocado seedlings, it was observed that after contact with the soil for 1 year, leaves of avocado

TABLE 3

*Yields and Fe, Mn, and Zn contents of bean plants grown in Experiment 1**

Number of FTE Product	FTE Application Rate				
	0 lb./A.	1000 lb./A.	4000 lb./A	10,000 lb./A	100,000 lb./A.
			Dry weight		
266	4.2	3.3	4.3	3.7	2.3
233A	4.2	3.0	2.7	3.7	1.3
253A	4.2	4.5	4.0	4.2	1.0
			Fe content		
266	65	66	68	77	68
233A	65	80	89	79	79
253A	65	69	63	69	60
			Mn content		
266	20	19	—	29	39
233A	20	20	18	17	19
253A	20	17	15	20	20
			Zn content		
266	42	32	61	52	69
233A	42	43	39	28	39
253A	42	35	38	40	35

* Yields in g./pot; Fe, Mn, and Zn contents in ppm. Average of three pots with three plants per pot.

plants grown on the FTE-treated soil contained considerably less Mn than did leaves grown on the control soils, even though the FTE contained Mn. The mean Mn value for seven control plants was 810 ppm., and for seven treated plants 105 ppm. The application rate was 33,000 pounds per acre. A pH check of the soil after the 1-year period indicated that the pH had been increased by the FTE application from about 6 to more than 7. This could have accounted for the decrease in Mn content of the avocado leaves and it might have been a factor for the high application rates in the two experiments described. This change in pH, of course, could not explain all the data, especially in the acid soil.

Experiment 2

The Fe59-tagged Fe contents of all the plant materials grown in soils containing the radioactive FTE product are given in table 4. With the possible exception of the second barley crop on the acid Sassafras soil, there was no uptake of Fe from the FTE at the rate of 50 pounds per acre. The plants receiving higher application rates contained only a very few parts per million. For the lemon cuttings generally less than 1 ppm. of the FTE Fe could be detected in any of the plants.

TABLE 4

Fe59-tagged Fe contents of plants grown in Experiment 2*

Soil	FTE Application Rate				
	50 lb./A.	200 lb./A.	1000 lb./A.	5000 lb./A.	15,000 lb./A.
			Barley, first crop		
Sassafras	0.0	2.4	1.4	—†	—†
Hanford	0.0	0.0	1.9	2.6	1.8
Sorrento	0.0	0.0	3.6	5.3	5.8
			Barley, second crop		
Sassafras	?	1.4	3.6	8.4	—†
Hanford	0.0	0.0	3.7	5.4	—†
Sorrento	0.0	1.0	2.5	5.7	—†
			Soybean crop		
Sassafras	0 0	2.1	—†	—†	—†
Hanford	0.0	0.0	0.8	2.3	—†
Sorrento	0.0	0.0	1.5	3.8	—†
			Eureka lemon cuttings		
Sassafras	0.2	0.2	0.2	—†	—†
Hanford	0.2	0.2	0.2	1.1	—†
Sorrento	0.0	0.0	0.0	0.0	—†

* Results in ppm./g. dry weight of plant tops. Each value is the mean of three replicates. The lowest value that could be detected with confidence was about 0.6 ppm.

† Toxic treatments killed plants.

TABLE 5

Fe extracted by N *Na acetate in presence of 0.1 per cent chelating agent from soils of Experiment 2 treated with Fe59-tagged FTE equivalent to 15,000 lb. per acre*

pH of Extracting Solution	Fe from Soil	Fe from FTE	Soil Fe* / FTE Fe	FTE Fe Extracted
	ppm.	*ppm.*		%
Sassafras				
5	112	45	2.4	14.5
6	56	5.6	10.0	1.8
7	32	4.0	8.0	1.3
8	32	3.6	8.9	1.2
Hanford				
5	37	33	1.1	10.6
6	35	4.8	7.4	1.6
7	34	3.8	9.0	1.2
8	33	2.6	12.9	0.8
Sorrento				
5	30	27	1.1	8.7
6	27	4.8	5.7	1.8
7	22	4.0	5.5	1.8
8	19	3.6	5.1	1.6

* The ratio of (soil Fe/FTE Fe) in barley at the 5000 lb./A. of FTE was 10, 11, and 12, for Sassafras, Hanford, and Sorrento soils, respectively. For soybeans it was 126 and 36 for Hanford and Sorrento. For soybeans on Sassafras soil it was 70 at the 200 lb. rate.

For the soybeans and the first barley crop there seemed to be more uptake of Fe59 from the acid Sassafras soil than from the other soils at the 200-pound rate. This did not seem to be true for higher rates, where in some instances the highest Fe59 uptake was from the Sorrento soil.

The data for Fe leached from the soils receiving the 15,000-pound FTE rate are given in table 5. Although there was virtually no plant growth at this rate, the magnitude of Fe solubility from FTE in presence of soil indicated the possibility of plant uptake of Fe from this source had other materials not restricted growth so severely. At pH values of 6, 7, and 8 of the extracting solution, the FTE Fe was considerably less soluble than was a certain portion of the soil Fe. At pH 5 the amounts extracted were more nearly equal for the soil and the FTE sources. From data appended to table 5 for the ratios of soil Fe to FTE Fe in plants, one must conclude that the plant uptake of FTE Fe more closely resembles the extracts at pH 6, 7, and 8. These data, however, do not compare identical application rates.

The dry-weight yield of tops for each of the crops is given in table 6. In this experiment also, high rates of FTE application showed toxic effects, which were more pronounced for soybeans than for the other crops. There appeared to be a

TABLE 6

Yield of crops grown in Experiment 2*

Soil	Control	FTE Application Rate				
		50 lb./A.	200 lb./A.	1000 lb./A.	5000 lb./A.	15,000 lb./A.
First barley						
Sassafras	—	292	228	228	—†	—†
Hanford	—	300	342	305	345	255
Sorrento	—	252	237	248	237	292
Differences between means were not significant.						
Second barley						
Sassafras	590	532	535	697	598	—†
Hanford	1233	732	403	805	900	—†
Sorrento	593	862	1078	860	718	—†
L.S.D. between means was 221 at 0.05; and 298 at 0.01.						
Soybeans						
Sassafras	1127	1177	875	—†	—†	—†
Hanford	2198	2217	2358	1992	873	—†
Sorrento	2539	2623	2502	1970	485	—†
L.S.D. between means was 581 at 0.05; 783 at 0.01.						
Eureka lemon cuttings						
Sassafras	1268	1723	1795	277	—†	—†
Hanford	1885	2423	2200	1762	752	—†
Sorrento	2338	2493	2123	2710	1313	—†
L.S.D. between means was 615 at 0.05; and 807 at 0.01.						

* Results in mg. dry weight of plant tops. Each value is the mean of three replicates.
† Toxic treatments killed plants.

yield increase for the second barley crop as a result of the FTE application on the Sorrento soil, but this was not true for the first barley crop. Barley was certainly more tolerant to the conditions brought about by the FTE than were the other crops. Some difficulties in growing the second crop of barley were caused by a fungus growth from the decaying roots of the previous crop, which may have accounted also for some of the differences in yields obtained. Soybean yields definitely indicated that calcareous soil reduced the toxic effect of the FTE.

The total Fe, Mn, and B contents of the second barley and soybean crops are given in table 7. These data indicate that the FTE material supplied B or Mn or both to some, but not all, growing crops, for it was a behavior which varied with the soil and with the crop.

For the second barley crop the total Fe content substantiated that found by the Fe59 method, that is, relatively little Fe was absorbed from the FTE. With increasing application rates of FTE there were definite Mn increases in the barley

TABLE 7

*Fe, Mn, and B contents of the second barley and soybean crops in Experiment 2**

Soil	FTE Application Rate				
	0	50 lb./A.	200 lb./A.	1000 lb./A.	5000 lb./A.
Fe in second barley crop					
Sassafras	72	83	77	80	85
Hanford	81	76	68	57	62
Sorrento	62	81	67	67	67
Mn in second barley crop					
Sassafras	113	253	316	898	1502
Hanford	25	51	41	54	62
Sorrento	46	271	276	283	233
B in second barley crop					
Sassafras	103	191	399	941	2482
Hanford	33	29	60	216	661
Sorrento	46	79	67	246	487
Fe in soybeans					
Sassafras	76	134	148	—†	—†
Hanford	64	119	81	105	290
Sorrento	51	89	68	113	135
Mn in soybeans					
Sassafras	196	257	545	—†	—†
Hanford	42	30	29	28	48
Sorrento	41	26	36	42	68
B in soybeans					
Sassafras	54	74	127	—†	—†
Hanford	31	26	31	48	248
Sorrento	36	25	49	83	328

* Results in ppm. dry weight. Each value is the mean of three replicates.
† Toxic treatments killed plants.

on the acid Sassafras soil. In barley on the Sorrento soil, each application rate resulted in about the same content of Mn, which was considerably higher than that of the control. In the Sorrento soil, as a result, the 50-pound-per-acre rate supplied as much Mn in the barley as did the 5000-pound rate. The 15,000-pounds-per-acre rate was omitted for the second crop of barley. In the nearly neutral Hanford soil, in contrast to the other two soils, FTE appeared to have no effect on Mn uptake.

The B content of barley was increased by FTE applications on all soils but not

for all rates, and this varied with the soil. In the Sassafras soil even the low applications resulted in a considerable uptake of B. Barley on the Hanford soil was slightly higher in B at the 200-pound rate, and very much higher at the 1000-pound rate, than in the controls. The same situation generally occurred with the Sorrento soil. Up to the 5000-pound application rate, there was little or no toxicity to barley, which was killed by the 15,000-pound-per-acre rate.

As pointed out previously, injury from high application rates was more pronounced with soybeans than with barley. This was most noticeable on the acid Sassafras soil, which is low in calcium. Jones and Scarseth (5) reported that plants under conditions of low Ca nutrition have a low tolerance to B.

The total Fe content of the soybeans might lead one to suspect that the FTE had been effective in supplying Fe to the plants, especially at the high application rate on the Hanford soil (table 7). This, however, was not indicated by the Fe59 analyses, and one must look elsewhere for the explanation of increased total Fe contents. At the high application rates the plants were considerably stunted, and undoubtedly this stunting resulted in sufficient concentration of Fe within the plant to give apparent elevated Fe contents. That a soil-frit interaction might have caused an increased soil Fe uptake is another possibility. For this reason it was especially fortunate that Fe59 was used in this experiment to differentiate these effects.

On the Sassafras soil Mn content of soybeans was increased by FTE, but in the other two soils FTE was only slightly effective in supplying Mn to the soybeans and only at the highest application rates. The increase in B was not so great in soybeans as in the barley; except on the acid Sassafras soil, there were only doubtful increases at the 50- and 200-pound-per-acre rates. The probable source of the toxicity to soybeans was B, and soybeans were far less tolerant of B than was barley. The toxicity level of B to soybeans is 75 to 100 ppm., according to Goodall and Gregory (3), who also reported, after Eaton, that the toxicity level of barley is 219 to 1111 ppm. Mn might also explain yield decrease in the acid Sassafras soil, since it has been reported that for soybeans more than 200 ppm. Mn may be a toxic excess (3). Responses also varied among the soils. Specific causes of the variability of the soils in respect to these micronutrients should be a very interesting subject for investigation.

No micronutrient deficiencies were evident in the plants grown in the three soils used in Experiment 2, so yield increases could not be expected. Causes of yield increase on Sorrento are not clear. Perhaps materials like FTE could be best evaluated under conditions of micronutrient deficiencies.

The failure of the FTE materials to supply more than a token amount of Fe to plants, within the range of recommended application rates, is apparent. It has been adequately demonstrated that Fe from FTE products was available to plants in solution culture (11, 14–16). In the past, Fe amendments by soil application, however, have always encountered considerable difficulties. Fe is rapidly immobilized in soil, and for products like the FTE materials to supply Fe to plants satisfactorily, the contact between roots and FTE particle must be essentially perfect. The infinitesimal distance that an Fe ion must move in the soil might

result in its precipitation, even under certain acidic conditions. This strong fixation to which Fe is subject is less important for other micronutrients. Relatively satisfactory sources of micronutrients other than Fe already exist for agricultural crops. The use of Fe chelates, however, gives considerable promise in solving the Fe problem by keeping Fe soluble in the soil (10). Slowly available sources of Fe, such as the FTE products, could be more valuable, since they are not so subject to leaching from the soil as are the chelating agents.

One question which arises in the interpretation of the data is whether excess Mn might have accounted for the failure of plants to take up Fe from the FTE. The Mn-Fe interaction in plants has been known for some time (13). Despite the high Mn uptake in some treatments, Mn apparently did not interfere with the Fe uptake except possibly in the acid Sassafras soil. In Experiment 1, where two products containing Fe, but not Mn, were used, there was likewise little uptake of Fe.

SUMMARY

Relatively insoluble silicate materials, designated as FTE products, with which micronutrients had been mixed, fused, and then milled to a very small particle size were studied in glasshouse experiments. Various crop plants and widely different soils were employed, and in one of the studies radioactive Fe was incorporated into the FTE mixture before it was fused. The materials were not a satisfactory source of Fe. For some other micronutrients, at least Mn, B, and possibly Zn, there was more effective uptake by plants. Responses varied among soils and among crops. Extremely high application rates of several thousand pounds of FTE an acre resulted in a decreased Mn uptake by avocado seedlings. The solubility in different reagents of micronutrients from some FTE products was given.

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TITRATION OF CLAY MINERALS

J. REX GOATES, KENNETH H. ANDERSON, AND CONRAD P. WILLIS

Brigham Young University[1]

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Failure of early investigators to find simple equilibrium constant expressions for titrations of clay minerals demonstrates the complexity of these reactions which could be due (*a*) to extreme heterogeneity in a single type of acid site; (*b*) to the existence of more than one type of site, each of which is fairly homogeneous; or (*c*) to a combination of (*a*) and (*b*).

An organic solvent in the titrations has been used in an attempt to detect separate titration reactions (4). Over the range of these titratious, two definite reactions were observed, each of which indicated fairly homogeneous acid sites. This supports proposition (*b*) and gives, therefore, some hope of eventually making a satisfactory thermodynamic analysis of titration data. The first step, of course, is to identify with certainty the reactions involved.

Titration data for six systems, involving three clays, are reported in the present study. Two montmorillonite-type clays (Wyoming bentonite and Texas Dunlap) and a kaolinite-type (Wakefield clay) were used. Wakefield is an English China clay found near St. Austell, Cornwall, England.

METHODS

Electrodialyzed clays

Clay particles in the size range 80–280 mμ were separated from the bulk samples by means of a Sharples supercentrifuge; they were then electrodialyzed and suspended in distilled, CO_2-free water. Aliquots of the stock suspensions were pipetted into 100-ml. Pyrex glass tubes fitted with neoprene stoppers. Varying amounts of standardized NaOH or KOH solutions were added, and the total volume of each was made up to 80 ml. with distilled, CO_2-free water. The samples were rocked gently in a 25 $\pm$ 0.02°C. water bath for 18 hours, a length of time found by preliminary experiments to be sufficient for establishing equilibrium. After being equilibrated, the samples were analyzed for Na^+ or K^+ activity by means of clay membrane electrodes of the type described by Marshall and coworkers (7, 8, 9, 10), and for H^+ activity with a glass electrode.

H^+-clays

The H^+-saturated samples were prepared by leaching with *M* $NH_4HC_2O_4$ [to complex with adsorbed Al^{+++} (12)], washing with distilled water until free of $C_2O_4^{=}$, and columning through Amberlite IR-120-H^+ analytical grade resin.

The degree to which the adsorbed Al^{+++} was removed by this treatment was determined by shaking samples of the clays for 10 minutes with *M* $BaCl_2$ solutions that had been adjusted to pH3, and then centrifuging and analyzing the

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decantate for Al^{+++} (13). The extracting solution was acidified to prevent precipitation of the displaced Al^{+++} as hydrous aluminum oxide. Less than 0.01 me. of Al^{+++} per 100 g. of clay was found. Similar treatment extracted 7- to 10-mg. ionic weights of Al^{+++} from samples that had been (*a*) columned only, or (*b*)

TABLE 1

Titration of clay minerals

Base Added per 100 g. Mineral	pH at Equilibrium	Activity of Metallic Ion at Equilibrium
me.		$a \times 10^{-4}$
Electrodialyzed Wyoming bentonite with KOH (0.8 per cent suspension)		
44.3	6.01	1.05
66.4	6.72	2.42
78.2	7.07	3.56
89.2	8.10	4.33
100.3	9.25	4.50
111.4	9.88	11.5
133.5	10.73	23.1
155.6	11.13	32.8
Electrodialyzed Texas Dunlap clay with KOH (0.8 per cent suspension)		
24.1	5.30	0.95
48.3	6.52	1.40
72.4	7.35	2.98
107.1	9.43	5.91
141.7	10.58	14.8
Electrodialyzed Wakefield clay with KOH (5.9 per cent suspension)		
1.80	7.25	1.08
2.29	7.70	1.89
2.62	8.39	3.06
2.79	8.69	3.06
2.95	8.91	3.69
3.11	9.14	4.15
3.28	9.34	4.88
3.60	9.61	6.00
3.93	9.85	6.92
Electrodialyzed Wakefield clay with NaOH (5.9 per cent suspension)		
1.42	7.13	1.60
1.90	7.80	2.21
2.37	8.72	3.50
2.61	9.26	3.82
2.79	9.58	4.17
2.98	9.72	5.64
3.17	9.90	6.11
3.36	9.95	6.68
3.55	10.11	7.25
4.03	10.30	9.65

TABLE 1—*Continued*

Base Added per 100 g. Mineral	pH at Equilibrium	Activity of Metallic Ion at Equilibrium
me.		$a \times 10^{-4}$
H^+-Wyoming bentonite with NaOH (0.6 per cent suspensions)		
00.0	3.40	—
20.1	4.10	—
35.2	4.70	0.84
42.5	4.98	1.09
65.4	7.50	1.41
80.4	9.62	4.07
88.0	10.07	8.34
96.2	10.42	14.7
110.6	10.84	20.9
H^+-Wakefield clay with NaOH (3 per cent suspensions)		
0	4.21	—
1.48	6.80	1.23
1.91	7.45	1.70
2.12	7.72	1.94
2.33	7.96	2.10
2.54	8.20	2.45
2.75	8.58	2.81
2.97	8.93	3.23
3.18	9.12	3.55
3.39	9.48	4.06
3.60	9.59	4.88
3.81	9.82	5.50

shaken with *M* HCl solutions for short periods and then washed free of HCl with successive portions of ethanol, acetone, and benzene.

NH_4^+ could not be detected with Nessler's reagent in a $BaCl_2$ extraction of the finished sample.

RESULTS AND INTERPRETATIONS

Electrodialyzed clays

Table 1 records the titration data. Figures 1 and 2 are typical of the results obtained by plotting the data according to an equation developed by Cook *et al.* (2) for expressing cation-exchange data. When written for the titration of a clay by NaOH, this equation is:

$$\frac{1-\theta}{\theta}\cdot a_{Na^+}\cdot a_{OH^-} \qquad \frac{\ }{K_4'}(a_{OH^-}+K_0) \tag{1}$$

The symbol θ is the fraction of S_0 (the number of possible adsorption sites) occupied by Na^+. S_0 and θ were calculated in the manner described by Cutler and Cook (3). K_4' is an apparent equilibrium constant (activity coefficients neglected) for the adsorption of Na^+ by a charged site, and the a's are activities.

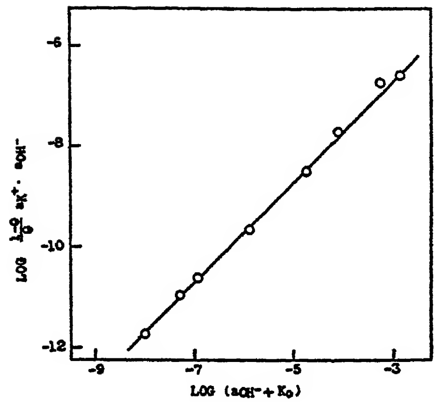

Fig. 1

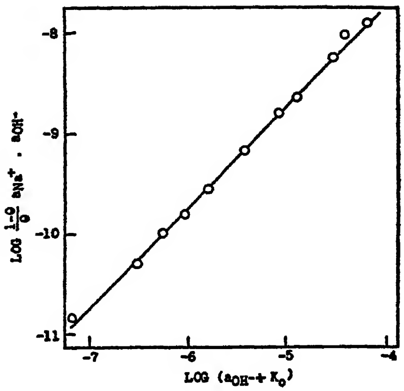

Fig. 2

Fig. 1. Titration of Electrodialyzed Wyoming Bentonite with KOH; Plotted According to Equation (*1*)

Fig. 2. Titration of H^+-Wakefield Clay with NaOH; Plotted According to Equation (*1*)

TABLE 2

Constants of equation (1) *for titration of clay minerals*

Clay	Base	S_0	$K'_4 \times 10^3$	$K_0 \times 10^{-9}$
Electrodialyzed				
Wyoming bentonite.....	KOH	120	5	7
Texas Dunlap...........	KOH	120	4	1
Wakefield..............	KOH	3	10	9
Wakefield..............	NaOH	3	4	8
H^+-saturated				
Wyoming bentonite.....	NaOH	90	16	1
Wakefield..............	NaOH	3	6	5

K_0 consists of a group of constants that depend on the nature of the acidic sites on the mineral. The logarithm of equation (*1*) is plotted to accommodate the wide range of values of $a_{Na^+} \cdot a_{OH^-}$. The solid lines in figures 1 and 2 are the unit slope lines required by the equation; the circles are the experimental values. It can be seen that the equation adequately describes the experimental data over the entire range of the titration.

Table 2 summarizes the values of the constants of equation (*1*) for the four systems studied. The K'_4 values are in general agreement with those reported by Cook *et al.* (2). The K'_4 values given in table 2 correspond to standard adsorption potentials of approximately 5 kcal. negative, which is reasonable for an average value of diffuse double-layer adsorption. The values of K_0 are also in general agreement with those previously reported (2). The thermodynamic significance of K_0 depends on the nature of the reactions that take place in the titration.

The systems involving electrodialyzed clays are undoubtedly complex, but at least the following equilibriums would seem to play a part in the reaction:

$$X^-\text{—}H^+ \rightleftarrows X^- + H^+ \tag{2}$$

$$X_3^-\text{—}Al^{+++} \rightleftarrows 3X^- + Al^{+++} \tag{3}$$

$$X^- + Na^+ \rightleftarrows X^-\text{—}Na^+ \tag{4}$$

$$H^+ + OH^- \rightleftarrows H_2O \tag{5}$$

$$Al^{+++} + 3\,OH^- \rightleftarrows Al(OH)_3 \tag{6}$$

$$Al(OH)_3 + OH^- \rightleftarrows Al(OH)_4^- \tag{7}$$

$$X_{(6)} + OH^- \rightleftarrows X_{(4)}^- \tag{8}$$

$$\begin{array}{c}|\\ \text{—SiOH}\\ |\end{array} \rightleftarrows \begin{array}{c}|\\ \text{—SiO}^-\\ |\end{array} + H^+ \tag{9}$$

The symbol X^-—H^+ in reaction (*2*) expresses the experimental observation that exchangeable H^+ is found on electrodialyzed clays. With *M* $BaCl_2$ as the leaching solution, we found by titration of the leachate that 58 per cent (70 me./100 g.) of the S_0 value of electrodialyzed Wyoming bentonite could be accounted for by adsorbed H^+.

Paver and Marshall (11), and more recently Schofield (12) and Harward and Coleman (6), emphasized the fact that electrodialyzed clays contain appreciable quantities of adsorbed Al^{+++}. Reaction (*3*) is intended to represent this information, although the reaction as written is probably an oversimplification. Al^{+++} has a strong tendency to hydrolyze to hydrous aluminum oxide even at low pH values. The form of the adsorbed aluminum might well be X^-—$Al^+(OH)_2$ or X_2^-—$Al^{++}(OH)$(depending on the pH), analogous to the hydrolyzed forms of adsorbed Fe^{+++} postulated by Bower and Truog (1).

Colorimetric determinations of Al^{+++} displaced from electrodialyzed Wyoming bentonite by acidified $BaCl_2$ solution showed 13-mg. ionic weights of Al^{+++} present per 100 g. of clay. Four successive extractions of 0.5 g. of the clay were made with 50-ml. portions of the *M* extracting solution. The first extraction removed 90 per cent of the total, and the fourth extraction removed slightly more than 1 per cent of the total.

Reaction (*4*) is the equilibrium reaction for the adsorption of Na^+ in the diffuse double layer. Reaction (*5*) is that of the base with the Arrhenius acid, H^+. Reaction (*6*) can be thought of as an analogous reaction involving the Lewis acid, Al^{+++}. With 13-mg. ionic weights of Al^{+++} present on the electrodialyzed bentonite, 13 millimoles of $Al(OH)_3$ would form.

This $Al(OH)_3$ represents another source of acidity, since it can be titrated to the aluminate ion (reaction *7*). To complete this reaction would require 13 additional me. of base. This 13 me. of base does not, however, contribute to the S_0 value, since Na^+ is not involved in this reaction. Reaction (*7*) would, of course,

affect the $(OH)^-$ concentration and the shape of the pH curve. In figure 3, (A) indicates the titration of a dilute solution of $AlCl_3$. The first inflection represents the equivalence point in the titration of Al^{+++} to $Al(OH)_3$; the second inflection, the completion of reaction (*7*). It can be seen that this reaction assumes importance in the range of pH 7 to 10.

Reaction (*8*) comes from the Cook *et al.* theory of the origin of the negative charges on clays. $X_{(6)}$ represents a 6-coordinated Al group, which, by reaction with OH^-, breaks off water and shifts to a 4-coordinated Al site with a negative charge. This shift in structure from octahedral to tetrahedral aluminum can take place at the exposed edges of the crystal with little rearrangement of the surface structure. The reaction is analogous to (*7*) except that in reaction (*8*) aluminum is still a part of the lattice. Regardless of whether reaction (*8*) is significant at low pH values, as was postulated by Cook *et al.*, it seems reasonable to expect that it would be important at the higher pH values, approximately in the range pH 7 to 10, as is true of reaction (*7*).

Unlike reaction (*7*), however, reaction (*8*) does make possible a negative site for the adsorption of a cation. The number of such sites will be a function of the pH. Reaction (*8*) may account, therefore, for the well-known observation that the base-exchange capacity of a clay is a function of the pH of the leaching solution used.

Reaction (*9*) represents the ionization of a silicic acid type of site produced by reaction of "broken" Si-O bonds with the solvent. In pure silica, these sites contribute appreciably to the base-exchange capacity only at very high pH values and do not have characteristics similar to those of the acid sites on clays. For example, equilibrium constants for the titration of silica in ethanol are several orders of magnitude smaller than for clays (5). This dissimilarity is also evident in titrations in water solutions. Since the value of the K_0 constant is related to the nature of the acidity of the mineral surfaces, there seems to be little evidence that reaction (*9*) represents a principal source of acidity in clays.

H^+-clays

The titration data for H^+-Wyoming bentonite and H^+-Wakefield are in table 1. The titration curve for the bentonite is plotted (B) in figure 3, where it can be compared with the electrodialyzed bentonite (C). Both curves show the inflection at about pH 7.5. The general shape of the H^+-clay, especially in the low pH range, is much more typical of the titration of a soluble weak acid than is that of the electrodialyzed H^+-Al^{+++}-clay.

By extracting a sample of the H^+-bentonite with $BaCl_2$, and titrating the displaced H^+, we obtained 63 me. of H^+ per 100 g. of clay, which corresponds well with the 65 me. of base required to reach the inflection point in the titration of the clay. The inflection point, therefore, marks the end of the titration of adsorbed H^+. Some reaction, however, involving both OH^- and Na^+ continues above the inflection, as can be seen from plots such as figure 4, which is typical of both electrodialyzed and H^+-clays. The equivalence point represents only about two thirds of the S_0 value of the H^+-saturated montmorillonite, as is shown in figure 4. The same is true of the H^+-saturated kaolinite.

Any proposed mechanism for the titration of an H^+-clay must fulfill at least three requirements: (*a*) it must account for the typical Arrhenius type acid titration curve; (*b*) it must account for reaction of the base and adsorption of the cation beyond the inflection point; and (*c*) it must have reasonable values for the thermodynamic constants that are associated with the proposed reactions.

Absence of adsorbed aluminum in these systems eliminates consideration of reactions (*3*), (*6*), and (*7*). Omitting also reaction (*9*) for reasons already discussed, we propose reactions (*2*), (*4*), (*5*), and (*8*) as the mechanism of the titration. Requirement (*a*) is met by reaction (*2*); requirement (*b*), by reaction (*8*). In kaolinites, in which there is little evidence of isomorphic substitution, reaction (*8*) may very well be the principal source of the charge on the clay.

The Cook *et al.* equation is convenient for obtaining information about the third requirement. K_0 of this equation for a mechanism involving reactions (*2*), (*4*), (*5*), and (*8*) can be shown to be approximately equal to $K_w/K_2' + 1/K_8'$ (activity coefficients neglected). K_w is the ion product constant of water, and K_2' and K_8' are the apparent equilibrium constants of reactions (*2*) and (*8*), respectively. As can be seen in table 2, the value of K_0 is of the order of 10^{-9}. This means that the minimum value of K_2' would be of the order of 10^{-5}. The minimum value for K_8' would be 10^9. K_4' for these titrations is of the order of 10^8. Unfortunately, to check these figures, we have no data for K_2', K_4', and K_8' obtained independently

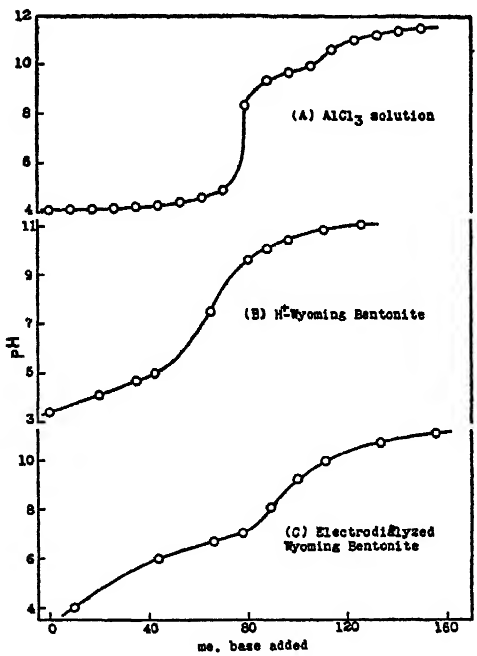

FIG. 3

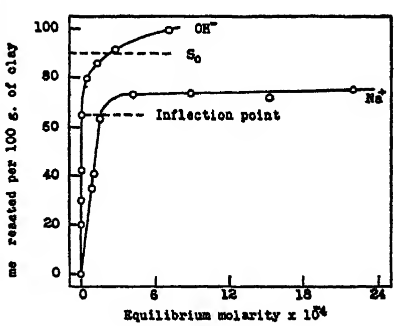

FIG. 4

FIG. 3. TITRATION CURVES FOR $AlCl_3$ AND WYOMING BENTONITE
FIG. 4. ADSORPTION OF Na^+ AND REACTION OF OH^- AS A FUNCTION OF THEIR EQUILIBRIUM CONCENTRATIONS IN THE SYSTEM H^+-WYOMING BENTONITE-NaOH

of the theory. The magnitudes of the values estimated from the theory do, however, seem plausible for the type of reactions postulated. For example, $K_8' = 10^9$ corresponds to a minimum adsorption potential for the OH^- of 11 kcal., a reasonable value for chemisorption; $K_4' = 10^3$ corresponds to an adsorption potential of about 4 kcal., which is reasonable for a diffuse double-layer potential; and $K_2' = 10^{-5}$ as a minimum value is in agreement with the value of 4×10^{-5} for the Wyoming bentonite, and 0.5×10^{-5} for Wakefield clay obtained by calculating K_2' from the pH of water suspensions of the H^+-clays.

SUMMARY

Titration data for six systems of electrodialyzed and H^+-saturated clays were made. The data include metallic cation activities as well as pH values. Eight possible reactions of the over-all titration mechanism of electrodialyzed clays are discussed. Of these eight, four are considered pertinent in the titration of the more simple H^+-clay systems. These reactions account for the inflection in the pH curves, and for the reaction of the base and adsorption of the cation above the inflection point. The data are adequately described by the Cook *et al.* equation, which made possible the estimation of some of the thermodynamic properties of the reactions postulated. Reasonable values for these properties are obtained, which lends support to the proposed mechanism.

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MEASUREMENT OF HYDRAULIC CONDUCTIVITY BY THE AUGER HOLE METHOD IN ANISOTROPIC SOIL

M. MAASLAND

Commonwealth Scientific and Industrial Research Organization[1]

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The auger hole method for measuring the hydraulic conductivity of homogeneous isotropic soil, described in several papers (4, 6, 7, 11[2]), utilizes the fact that if an auger hole is made in the soil extending below the water table and water is removed from the hole, the hole will refill at a rate determined by the hydraulic conductivity of the soil, the dimensions of the hole, and the height of water in the hole.

In the formulas and graphs which have been derived and prepared (4, 5, 6, 7, 11[2]) the soil is assumed to be isotropically uniform. With the aid of these formulas and graphs the hydraulic conductivity is calculated from measured rates of rise in auger holes.

The purpose of this paper is to modify the aforementioned formulas to permit calculation of the horizontal and vertical hydraulic conductivity of anisotropic soil, K_h and K_v respectively, from measured rates of rise, assuming the quotient K_h/K_v to be known. The error resulting from the assumption of isotropicity of the soil can then be evaluated. It will also be possible to determine the components K_h and K_v by suitably combining an auger hole measurement with a tube or piezometer measurement (3, 4, 7) at the same depth and location of the soil.

AVAILABLE FORMULAS FOR ISOTROPIC CONDITIONS

Kirkham (5) gives a general formula for flow into auger holes (fig. 1) and into cavities below piezometers:

$$dQ/dt = KA(d - h) \tag{1}$$

or

$$K = \frac{\pi r^2}{A(d - h)} \frac{dh}{dt} \tag{1a}$$

where K = hydraulic conductivity; r = radius of hole; d = depth of hole below ground-water table; h = depth of water in hole during measurement; dQ/dt = quantity of flow entering the system per unit time; dh/dt = rate of rise in auger hole or piezometer; and A = a constant for a given flow geometry.

The factor A may be defined as a factor which, when multiplied by the hydraulic conductivity and by the piezometric head across the system, yields the

[1] Commonwealth Research Station, Merbein, Victoria, Australia.

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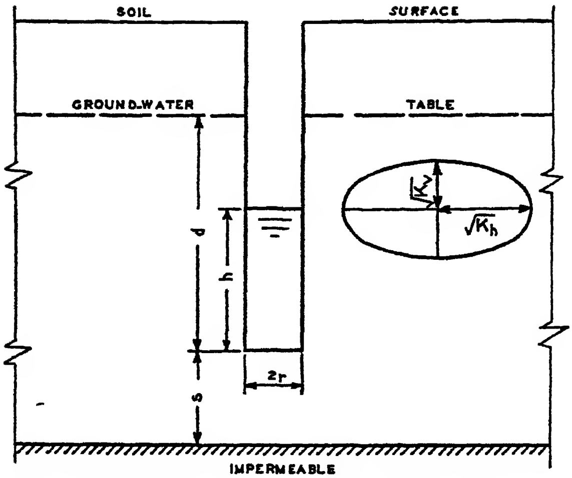

FIG. 1. AUGER HOLE IN ANISOTROPIC SOIL; $K_h/K_v = 4$

total quantity of flow per unit time entering or leaving the system. Dachler (2) uses the term Formfactor for this factor, Hvorslev (3) calls it a shape factor, and others sometimes simply use the term A factor. The expression "effective hemispherical radius" used by Zangar (14) is a slightly different concept from our A factor (his effective hemispherical radius $= A/2\pi$). Hvorslev (3) lists various shape factors for flow into piezometers which take anisotropy into account. A has the dimension of length.

For auger holes in homogeneous isotropic soil we have:

$$A = rf(d/r, h/r, s/r) \tag{2}$$

In the formula s is the depth of the bottom of the hole above the impermeable layer. Where the hole just reaches an impermeable layer ($s = 0$, fig. 1) or—which is identical—where the hole extends into the impermeable material, Kirkham and van Bavel (6) derived an analytical expression for A. In the latter case, d is the depth measured from the ground-water table to the impermeable layer. For $s \to \infty$ (or, for practical purposes, $s \geq d$), constants were determined by Ernst[2] from relaxation drawings. Van Bavel and Kirkham (11) reported some A values for cases where $0 < s < d$.

In a homogeneous isotropic soil we find for $s = 0$ [see formula 5 of van Bavel and Kirkham (11)]:

$$A = \frac{16rd}{\pi(d-h)}\left[\cos\left(\frac{\pi h}{2d}\right)\cdot\frac{K_1\left(\frac{\pi r}{2d}\right)}{K_0\left(\frac{\pi r}{2d}\right)} - \frac{1}{3^2}\cos\left(\frac{3\pi h}{2d}\right)\cdot\frac{K_1\left(\frac{3\pi r}{2d}\right)}{K_0\left(\frac{3\pi r}{2d}\right)} + \frac{1}{5^2}\cos\left(\frac{5\pi h}{2d}\right)\cdot\frac{K_1\left(\frac{5\pi r}{2d}\right)}{K_0\left(\frac{5\pi r}{2d}\right)} - \cdots \text{etc.}\right] \tag{3}$$

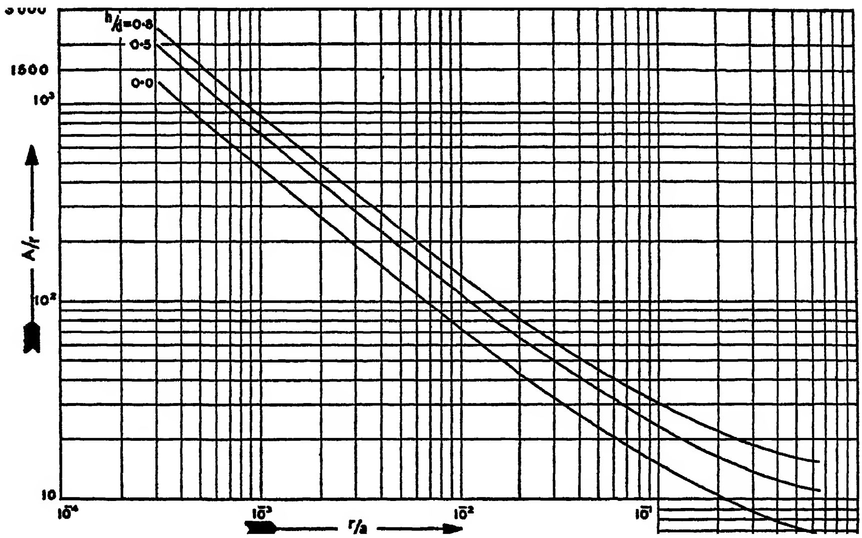

FIG. 2. VALUES OF A/r AGAINST r/d FOR $h/d = 0.8$, 0.5, AND 0.0, RESPECTIVELY; $s = 0$

Here K_0 and K_1 are Bessel functions of the second kind of zero and first order, respectively; this K_0 must not be confused with the arbitrary constant K_0 introduced later.

Calling the last factor of the right term $F(h/d, r/d)$, we have:

$$A = \frac{16rd}{\pi(d - h)} F(h/d, r/d) \tag{4}$$

Values of A/r are plotted against r/d in figure 2 for $h/d = 0.8, 0.5, 0.0$, respectively; $s = 0$. The plotted values have been calculated from (3).

For $s \to \infty$, A is again independent of s, as in the case where $s = 0$. Since an analytical solution for this case was not available at the time this paper was prepared, the constants reported by Ernst[2] were used for evaluating the influence of anisotropy for $s \to \infty$. Equation (3) was modified to evaluate the influence of anisotropy for the case that $s = 0$.

THEORY OF WATER MOVEMENT IN HOMOGENEOUS ANISOTROPIC MEDIA

In determining the needed modifications, results of general theory on fluid flow in anisotropic media were utilized. Pertinent theory was described by Versluys (12), Dachler (1, 2), Vreedenburgh (13), Muskat (9), and Maasland and Kirkham (8). The theoretical results depend on the validity of Darcy's law, which is assumed to be applicable. The three principal results are, for convenience, expressed here as theorems, which were taken from Maasland and Kirkham (8). In these theorems, the expression "hydraulic conductivity" was substituted for "air permeability", since now, instead of air flow, water movement through saturated soil is being considered.

Theorem I

An anisotropic soil may be replaced by an equivalent, fictitious, porous mass of equal size, with three mutually perpendicular, uniquely directed systems of pore tubes. In this fictitious mass the net flow per unit area is the same in every direction as in the actual soil, provided the hydraulic head is the same everywhere in the fictitious medium as in the actual soil. The three unique, mutually perpendicular directions are called the principal directions x, y, and z of anisotropy; and, for the most general case, three unique values of hydraulic conducivity K_x, K_y, and K_z correspond to these directions. For the special case that $K_x = K_y$, and with K_z not equal to K_x or K_y, the principal directions x and y are replaced by a principal plane perpendicular to the direction z; this latter direction then remains alone as a unique principal direction.

Theorem I, as applied to water movement in porous media, is due apparently to Versluys (12). The corresponding theorem occurs in electricity in the case of an anisotropic dielectric [for a concise treatment, see, for example, Smythe (10)].

Theorem II

The effect of an anisotropy in the hydraulic conductivity is equivalent to the effect of a shrinkage or expansion of the coordinates of a point in the flow system. That is, one can, by suitably shrinking or expanding the coordinates of each point in an anisotropic medium, obtain an equivalent, homogeneous, isotropic system. A proof of theorem II is given by Dachler (1, 2) for two-dimensional flow and by Maasland and Kirkham (8) and Vreendenburgh (13) for three-dimensional flow.

Let K_x, K_y, and K_z be, respectively, the hydraulic conductivities in the principal directions x, y, and z (Theorem I). Now let K_0 be an arbitrary constant with the dimensions of K_x, K_y, and K_z; then x', y', and z' of the transformed systems are defined by:

$$x' = (K_0/K_x)^{\frac{1}{2}}x \tag{5}$$

$$y' = (K_0/K_y)^{\frac{1}{2}}y \tag{6}$$

$$z' = (K_0/K_z)^{\frac{1}{2}}z \tag{7}$$

Theorem III

The hydraulic conductivity K, for the equivalent homogeneous isotropic medium into which the anisotropic medium may be expanded or shrunk (theorem II), is related to the hydraulic conductivities of the actual anisotropic system by the relation

$$K = (K_xK_yK_z/K_0)^{\frac{1}{2}} \tag{8}$$

where K_0 is the arbitrary constant, and K_x, K_y, and K_z are the hydraulic conductivities for the principal directions (theorem I) of the actual anisotropic medium. For a proof of theorem III, see (8, 13).

APPLICATION OF THE THEORY TO AUGER HOLES

In the present application, we assume that the principal directions of anisotropy coincide with the horizontal and vertical directions, and also that there is no anisotropy in the horizontal plane. We can then take:

$$K_x = K_y = K_h \text{ and } K_z = K_v \tag{9}$$

From *(5)*, *(6)*, *(7)*, and *(9)* we find, for the coordinates (x', y', z') of a point P' in an equivalent isotropic medium into which a point P of coordinates (x, y, z) in the actual anisotropic medium is to be transformed, that:

$$x' = (K_0/K_h)^{1/2}x;\ y' = (K_0/K_h)^{1/2}y;\ \text{and } z' = (K_0/K_v)^{1/2}z \tag{10}$$

From *(8)* and *(9)* we find, for the equivalent hydraulic conductivity in the transformed medium, the result:

$$K = (K_hK_hK_v/K_0)^{1/2} \tag{11}$$

As the axis of the auger hole coincides with the vertical direction, we find from *(10)* that the circular cross section of the auger hole remains circular, and that in the fictitious medium the radius of the hole becomes $r' = (K_0/K_h)^{1/2}r$. It is then found from *(2)* and *(10)* that in case of anisotropy:

$$A_a = (K_0/K_h)^{1/2}rf\{(K_h/K_v)^{1/2}(d/r),\ \ (K_h/K_v)^{1/2}(h/r),\ \ (K_h/K_v)^{1/2}(s/r)\} \tag{12}$$

or

$$A_a = (K_0/K_h)^{1/2}A_a' \tag{13}$$

The subscript a of A_a and of A_a' denotes the condition of anisotropy. A_a' is the "anisotropic A factor" for the transformed system in which $r' = r$. The difference between A_a' in *(13)* and A in *(2)* lies in the fact that A_a' in equation *(13)* contains the additional factor $(K_h/K_v)^{1/2}$ for each of the three terms in the functional expression.

From *(4)* and *(10)* we find for $s = 0$:

$$A_a = (K_0/K_h)^{1/2}\,\frac{16rd}{\pi(d-h)}\,F\{h/d,\ (K_v/K_h)^{1/2}(r/d)\} \tag{14}$$

which again can be written as:

$$A_a = (K_0/K_h)^{1/2}A_a' \tag{13}$$

For the rate of inflow under anisotropic conditions we find from *(1)*, *(11)*, and *(12)*:

$$dQ/dt = (K_hK_hK_v/K_0)^{1/2}\,A_a(d-h)$$

or, replacing *(12)* by *(13)*:

$$dQ/dt = (K_hK_hK_v/K_0)^{1/2}(K_0/K_h)^{1/2}A_a'(d-h)$$

or

$$dQ/dt = (K_hK_v)^{1/2}A_a'(d-h) \tag{15}$$

In equation (*1*) $(d - h)$ is not affected by the transformation (see theorem I) as this is not a geometric factor but a factor which denotes the hydraulic head across the system. It will be remembered that the hydraulic head is defined in units of height of water, and that these units usually coincide with the units of length used in defining the geometric properties of the flow medium.

From equation (*15*) we observe that the rate of inflow into the hole (dQ/dt) is independent of the value of the arbitrary constant K_0—as it should be.

The total inflow into a hole should be, and usually is, sufficiently small during the period of measurement with the auger hole method to permit calculation of the hydraulic conductivity on the basis of an average hydraulic head and, consequently, a constant value of the A factor (4, 7, 11[2]). An example of calculating the hydraulic conductivity follows.

Assume $r = 0.2$ feet, $d = 2.5$ feet, $h = 1.25$ feet, $s = 0$, $dh/dt = 0.1$ foot/25 seconds, and $K_h/K_v = 1$ (isotropy). Figure 2 gives values of A/r for $s = 0$ which have been calculated from equation (*3*). From this figure we can obtain the A value needed for the example. We have $r/d = 0.08$, $h/d = 0.5$, and find that $A/r = 26.8$. From equation (*1a*) it follows that:

$$K = \frac{\pi r^2}{(d - h)A} \cdot \frac{dh}{dt} = \frac{\pi(0.2)}{(1.25)(26.8)} \cdot \frac{0.1}{25} = 0.75 \times 10^{-4} \text{ ft./sec.} = 6.45 \text{ ft./day}$$

If the measurement is made in an anisotropic soil this calculated value of K will be an apparent hydraulic conductivity, which can be denoted as K_{apparent}. The apparent hydraulic conductivity can be defined as that hydraulic conductivity which is found when isotropy is assumed. We rewrite equation (*1*) as follows:

$$dQ/dt = K_{\text{apparent}}\, A(d - h) \tag{16}$$

Substitution of (*15*) in (*16*) gives:

$$(K_h K_v)^{\frac{1}{2}}/K_{\text{apparent}} = A/A_a' \tag{17}$$

or, multiplying both sides of (*17*) by $(K_h/K_v)^{\frac{1}{2}}$:

$$K_h/K_{\text{apparent}} = (K_h/K_v)^{\frac{1}{2}}(A/A_a') \tag{18}$$

We remember from equation (*13*) that A_a' is the "anisotropic A factor" for the fictitious isotropic system in which $r' = r$.

Assume now that this example of measurement was made in an anisotropic soil with $K_h/K_v = 100$. A_a'/r can then also be obtained from figure 2. It follows from equation (*14*) that we now need the (A/r) value for $h'/d' = h/d = 0.5$, and for $r'/d' = (K_v/K_h)^{\frac{1}{2}}(r/d) = 0.1 \times 0.08 = 0.008$, for which we find $A_a'/r = 133$. We calculate from (*17*) that in this example $(K_h K_v)^{\frac{1}{2}}/K_{\text{apparent}} = 26.8/133 = 0.201$, and from (*18*) that $K_h/K_{\text{apparent}} = 2.01$.

It is finally found that $K_h = 2.01\, K_{\text{apparent}} = 2.01 \times 6.45 = 12.9$ ft./day.

To interpret apparent values of hydraulic conductivity, certain curves and tables are useful. $(K_h K_v)^{\frac{1}{2}}/K_{\text{apparent}}$ has been plotted against $(K_h/K_v)^{\frac{1}{2}}$ in figure 3 for $r/d = 0.16, 0.08, 0.04$, and 0.02, respectively; $h/d = 0.5$ is constant for all

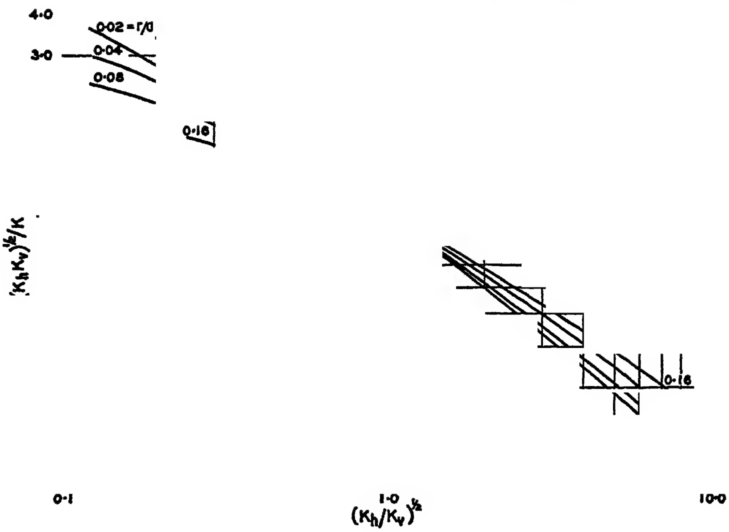

FIG. 3. VALUES OF $(K_hK_v)^{\frac{1}{2}}/K_{\text{apparent}}$ AGAINST $(K_h/K_v)^{\frac{1}{2}}$ FOR $r/d = 0.16$, 0.08, 0.04, AND 0.02; $h/d = 0.5$, AND $s = 0$

curves, and $s = 0$. These curves have been calculated by the aid of figure 2 and equations (*13*), (*14*), and (*17*). The calculations for this figure have been made in a manner similar to the one made in the above example.

Table 1 gives values of K_h/K_{apparent} for the same r/d values as in figure 3, and for $h/d = 0.8$, 0.5, and 0.0, respectively; $s = 0$. The values of K_h/K_{apparent}

TABLE 1

*K_h/K_{apparent} for various values of $(K_h/K_v)^{\frac{1}{2}}$, (r/d), and (h/d)**

r/d	h/d	K_h/K_{apparent}							
		$(K_h/K_v)^{\frac{1}{2}} = 0.125$	$(K_h/K_v)^{\frac{1}{2}} = 0.25$	$(K_h/K_v)^{\frac{1}{2}} = 0.5$	$(K_h/K_v) = 1$	$(K_h/K_v)^{\frac{1}{2}} = 2$	$(K_h/K_v)^{\frac{1}{2}} = 3.33$	$(K_h/K_v)^{\frac{1}{2}} = 5$	$(K_h/K_v)^{\frac{1}{2}} = 10$
0.16	0.8	—	0.40	0.66	1	1.41	1.75	2.04	2.53
	0.5	—	0.42	0.67	1	1.36	1.67	1.91	2.33
	0.0	—	0.44	0.69	1	1.38	1.67	1.91	2.33
0.08	0.8	0.28	0.44	0.71	1	1.33	1.58	1.79	2.13
	0.5	0.31	0.49	0.73	1	1.31	1.54	1.72	2.01
	0.0	0.32	0.50	0.73	1	1.28	1.50	1.69	1.96
0.04	0.8	0.35	0.53	0.75	1	1.26	1.44	1.61	1.86
	0.5	0.38	0.56	0.77	1	1.24	1.41	1.54	1.78
	0.0	0.39	0.57	0.78	1	1.24	1.39	1.53	1.77
0.02	0.8	0.42	0.60	0.79	1	1.26	1.35	1.48	1.67
	0.5	0.45	0.62	0.81	1	1.19	1.34	1.44	1.64
	0.0	0.46	0.63	0.81	1	1.18	1.32	1.43	1.62

* $s/d = 0$ for all cases.

TABLE 2

*Comparison of values of K_h/K_{apparent} for $s/d = \infty$ and $s/d = 0$**

r/d	s/d	K_h/K_{apparent}						
		$(K_h/K_v)^{\frac{1}{2}} = 0.25$	$(K_h/K_v)^{\frac{1}{2}} = 0.5$	$(K_h/K_v)^{\frac{1}{2}} = 1$	$(K_h/K_v)^{\frac{1}{2}} = 2$	$(K_h/K_v)^{\frac{1}{2}} = 3.33$	$(K_h/K_v)^{\frac{1}{2}} = 5$	$(K_h/K_v)^{\frac{1}{2}} = 10$
0.16	∞	—	—	1	1.48	1.90	2.14	2.82
	0	0.42	0.67	1	1.36	1.67	1.91	2.33
0.08	∞	—	0.67	1	1.38	1.68	1.92	—
	0	0.49	0.73	1	1.31	1.54	1.72	2.01
0.04	∞	0.49	0.72	1	1.29	1.51	—	—
	0	0.56	0.77	1	1.24	1.41	1.54	1.78

* $h/d = 0.5$ for all cases.

have been calculated by the aid of figure 2 and equations (*13*), (*14*), and (*18*). It follows from table 1 that if a measurement is made when removing an amount of water equivalent to a depth of $0.2d$, $0.5d$, and d, and if $K_h/K_v = 25$ and $r/d = 0.08$ (that is, for example, a 4-inch-diameter hole having an initial depth of water of 25 inches in static equilibrium), then $K_h/K_{\text{apparent}} = 1.79$, 1.72, and 1.69, respectively. From these figures and others given in table 1, we observe that the amount of water removed has only a slight influence on K_h/K_{apparent}. The influence of r/d is somewhat greater. For example, for values of $r/d = 0.16$, 0.08, 0.04, and 0.02, and if $K_h/K_v = 25$ and $h/d = 0.5$, we find for K_h/K_{apparent} the values 1.91, 1.72, 1.54, and 1.44, respectively. Table 1 shows clearly that the auger hole method is primarily a measure of the horizontal hydraulic conductivity component.

Some values of K_h/K_{apparent} have been calculated for $s = \infty$ by the aid of equations (*12*), (*13*), and (*18*). These values have been obtained from charts given by Ernst,[2] who determined constants for calculating the hydraulic conductivity from measurements in auger holes where the impermeable layer is entirely absent or at large depth below the bottom of the hole[3]. Ernst determined the constants for homogeneous isotropic conditions from relaxation drawings.

[3] Ernst (see footnote[2]) gives C values for computing the hydraulic conductivity from measured rates of rise. C is given by the following equation:

$$864 \frac{\pi r^2}{(d - h)A} \qquad (19)$$

of which the variables r, d, h, and A have all been defined previously. The hydraulic conductivity is computed from:

$$K = C(dh/dt) \qquad (20)$$

Because of the inclusion of the constant 864 in (*19*), K is found from in meters per day, if the rate of rise (dh/dt) is measured in cm./sec.

Ernst plotted C values on double-logarithmic paper for two radii (4 and 6 cm., respectively) and for various values of $(d - h)$ and d. Ernst's y equals our $(d - h)$ and his H

Clearly, the value of A'_a in this case is, as it was for $s = 0$, independent of s'. The results of the computations are given in table 2, which lists values of $K_h/K_{apparent}$ for $s/d = \infty$ and $s/d = 0$, respectively, while $h/d = 0.5$. For example, we find, for $r/d = 0.16$ and $K_h/K_v = 25$, that $K_h/K_{apparent} = 2.14$ and 1.91 for $s/d = \infty$ and 0, respectively. Table 2 shows that, in general, the influence of K_v is larger for $s/d = \infty$ than it is for $s/d = 0$ for the same value of $(K_h/K_v)^{\frac{1}{2}}$. This is to be expected because of the more vertically directed flow immediately around and through the bottom of the hole when $s/d \neq 0$. From figure 3 and the two tables we observe that the relative influence of K_v increases with decreasing r/d.

SUMMARY

Formulas have been derived for determining the influence of anisotropy on the auger hole method for measuring hydraulic conductivity. Values of $K_h/K_{apparent}$ have been computed, for some values of h/d and r/d that are likely to be of practical importance, from formulas given by Kirkham and van Bavel for $s = 0$, and from charts given by Ernst for $s = \infty$, after modifying the formulas and the charts to make them suitable for application to homogeneous anisotropic conditions. $K_{apparent}$ is defined as the apparent hydraulic conductivity which is calculated from a measurement when homogeneous isotropic conditions are assumed; s is the depth of the bottom of the hole above the impermeable layer; r is the radius of the hole; d is the depth of the hole below the ground-water table; h is the depth of water in the hole during the measurement; and K_h and K_v are the hydraulic conductivities in the horizontal and vertical directions, respectively.

It follows that the amount of water removed for measuring the rate of rise has little influence on $K_h/K_{apparent}$. For example, it is found for $s = 0$, $r/d = 0.04$, and $K_h/K_v = 10$, that $K_h/K_{apparent} = 1.44$, 1.41, and 1.39 for $h/d = 0.8$, 0.5, and 0.0, respectively.

The influence of r/d is somewhat larger. For $s = 0$, $K_h/K_v = 10$, and $h/d = 0.5$, we find that $K_h/K_{apparent} = 1.67$ and 1.34 for $r/d = 0.16$ and 0.02, respectively.

Comparison of quotients of $K_h/K_{apparent}$ shows that influence of the vertical component of hydraulic conductivity is more pronounced for $s = \infty$ than for

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equals our d. Values of C have been taken from those graphs for $h = 0.5d$, and by the aid of these values, A/r was computed from (19). The resulting (A/r) values were plotted in a manner similar to that in figure 2. Once A/r is obtained, $K_h/K_{apparent}$ is computed in a similar manner as in the previous example where $s = 0$.

An example of computing $K_h/K_{apparent}$ follows. Assume $r/d = 0.08$ and $h/d = 0.5$. From Ernst's graph for $s = \infty$ and an auger hole with a radius of 4 cm., we find for $d = 50$ cm. and $(d - h) = 25$ cm., that $C = 13.8$. From (*19*) we find that $A/r = 31.4$.

Assume now that the example of measurement was made in an anisotropic soil with $K_h/K_v = 25$. We then need the (A/r) value for $h'/d' = h/d = 0.5$, and $r'/d' = (K_v/K_h)^{\frac{1}{2}}(r/d) = 0.08/5 = 0.016$. That is, we now need the C value from Ernst's graph for $s = \infty$ and $r = 4$ cm., for $d' = 250$ cm. and $(d' - h') = 125$ cm., for which we find $C = 1.06$. From (*19*) we find that $A'_a/r = 81.8$. It follows from (*18*) that $K_h/K_{apparent} = (5)(31.4)/(81.8) = 1.92$, which value is listed in table 2 for $s/d = \infty$, $r/d = 0.08$, and $h/d = 0.5$.

$s = 0$. This is to be expected because of the more vertically directed flow immediately around and through the bottom of the hole when $s/d \neq 0$. For $r/d = 0.16$ and $K_h/K_v = 10$, we find that $K_h/K_{\text{apparent}} = 1.90$ and 1.67 for $s = \infty$ and $s = 0$, respectively.

The study shows that the auger hole method is primarily a method for measuring the horizontal hydraulic conductivity.

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SOILS OF THE NANAKHI SERIES, EAST PAKISTAN: II. CHEMICAL INVESTIGATION AND CLASSIFICATION

A. KARIM AND D. H. KHAN

Dacca University[1]

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An earlier paper on the soils of the Nanakhi series, East Pakistan, dealt with morphology, textural separates, and exchangeable cations (5). As noted therein the character of the soils of this area are truly pedogenic with a gray friable loamy surface and a red-brown clayey subsoil of granular structure. They are also moderately acid. The profiles are completely leached of carbonates, and the B horizons of the trough soils contain some iron concretions. Cation-exchange capacity ranges from 13 to 28 me per 100 g., the percentage base saturation showing a rise with depth. Exchangeable H^+ alone accounts for about 50 per cent of the total cation-exchange capacity. The parent materials of the soils were found to be heterogeneous in character.

The present paper deals with the chemical investigation and classification of these soils, which were subjected to total chemical analyses, determinations of different forms of iron oxide, and fusion analyses of the clay colloid and fine earth fractions.

The Nanakhi area represents a highland arc with conspicuous crests and troughs and a vegetation association of agricultural crops and native grass. The soil types as encountered in the present survey, with their location and vegetation are as follows:

Brownish gray fine sandy loam (bG FSL) Dark gray fine sandy loam (DG FSL)	Soils under grass cover—on the crest
Gray fine sandy loam (G FSL/1 and G FSL/2)	Cultivated soils—on the crest
Grayish yellow fine sandy loam (gY FSL) Yellowish gray fine sandy loam (yG FSL) Gray sandy loam (G SL)	Cultivated soils—in the trough

Two profiles of G FSL were studied because of the much wider occurrence of this type in the area surveyed. G SL, on the other hand, was not sampled for chemical investigation because its occurrence was limited to a few patches.

ANALYTICAL METHODS

The analytical methods followed those described by Piper (8), except for the determination of free Fe_2O_3, which followed Karim's (4) nascent hydrogen reduction method.

[1] Ramna, Dacca, East Pakistan.

Total soluble salts were determined by conductivity measurements of water suspensions of the soils; organic carbon, by Black and Walkley's wet oxidation method; total nitrogen, by Kjeldahl method; total phosphorus on an aliquot of the HCl extract of the fuse by colorimetric method; and total potassium on an aliquot of the HCl extract of the fuse by precipitating as cobaltinitrite and oxidizing the cobaltinitrite with $KMnO_4$.

Total Fe_2O_3 was determined on HCl extract of the fuse of soil and clay by $KMnO_4$ oxidation method (volumetrically); and free Fe_2O_3 by nascent hydrogen reduction method (4) employing Zn-dust and potassium-oxalate-oxalic acid solution buffered at pH 3.5. The combined Fe_2O_3 represented the fraction obtained by subtracting free Fe_2O_3 from total Fe_2O_3. The Fe_2O_3 (total, free, and combined) in noncolloid fraction was indirectly obtained by subtracting the different forms of Fe_2O_3 of clay from those of total soil.

Fusion analyses of soil and clay involved Na_2CO_3 fusion, double evaporation of the HCl extract of the fuse and dehydration, ignition, and purification by HF. Aluminum was obtained by deducting Fe and Ti, determined colorimetrically, from Fe, Ti, and Al, determined gravimetrically by precipitating as hydroxide and weighing as oxide.

TOTAL CHEMICAL ANALYSES

The total chemical analyses included determination of loss on acid treatment, total soluble salts, loss on ignition, organic carbon, total nitrogen, total phosphorus, and total potassium. The results are presented in table 1.

Loss on acid treatment. The 0.2 N HCl treatment employed dissolved most of the free sesquioxides, and thus the loss on acid treatment may roughly be regarded as a measure of free sesquioxides in pedalferic soils. Table 1 shows that the greatest loss occurred in the B_1 horizon—a feature which points toward a podzolic type of soil formation.

Total soluble salts. Though the amounts of total soluble salts (0.003–0.02 per cent) have virtually no quantitative significance, their distribution in the soils with respect to depth shows a relative enrichment in the deeper horizons. The low quantitative value of the total soluble salts is, however, in agreement with the relevant climatic factors and low pH values.

Loss on ignition. Since the loss on ignition depends on a number of factors, such as organic matter, $CaCO_3$, clay content, and also the hydration condition, nature, and relative abundance of the clay minerals, these soils did not exhibit any positive relationship between organic carbon and loss on ignition. On the other hand, the soils, most samples of which were of heavy texture, showed a positive correlation between clay content and ignition loss (table 1).

Organic carbon and nitrogen. The distribution of organic carbon and nitrogen showed similar trends down the profiles, irrespective of type, topography, and culture, which indicates a close relationship between the two components. The ratio narrows with depth, showing a relative enrichment of nitrogen in comparison with carbon. The general level of nitrogen and carbon content was noted to be higher in the virgin soils (particularly the surface horizons) than in the cultivated soils.

TABLE 1

Total chemical analysis of Nanakhi soils

Soil Type and Horizon	Depth	Loss on Acid Treatment	Total Soluble Salts	Loss on Ignition	Organic Carbon	Total Nitrogen	Total Phosphorus	Total Potassium
	in.	%	%	%	%	%	%	%
bG FSL								
A_{1a}	0–1	0.72	0.012	6.75	1.71	0.143	0.040	2.07
A_{1b}	1½–2½	1.08	0.007	6.94	1.49	0.126	0.040	2.04
B_1	4–7	2.01	0.010	8.62	0.97	0.101	0.043	1.96
B_2	10–17	1.85	0.009	9.95	0.58	0.073	0.030	2.51
B_3	20–35	0.20	0.003	9.18	0.36	0.037	0.028	3.19
DG FSL								
A_{1a}	0–¾	0.02	0.012	5.85	2.22	0.168	0.039	2.21
A_{1b}	1½–3½	0.54	0.006	4.79	1.07	0.081	0.037	1.82
B_1	4½–7½	1.46	0.008	7.33	0.62	0.070	0.042	2.95
B_2	9½–24	1.15	0.007	9.28	0.41	0.047	0.036	2.49
B_3	28–46	1.96	0.023	8.00	0.24	0.032	0.036	2.49
G FSL/1								
A	0–2	0.90	0.008	5.10	1.54	0.132	0.033	1.78
B_1	4–7	1.57	0.007	5.99	0.97	0.080	0.081	2.35
B_2	9–18	1.67	0.005	8.74	0.36	0.063	0.058	2.29
B_3	22–36	0.80	0.010	8.35	0.23	0.056	0.039	2.27
G FSL/2								
A	0–1½	0.44	0.009	4.76	1.14	0.096	0.034	2.08
B_1	3–8	1.93	0.007	7.25	0.87	0.083	0.052	1.92
B_2	10–20	1.72	0.008	9.28	0.40	0.063	0.052	2.11
B_3	23–37	1.72	0.012	7.65	0.26	0.053	0.024	3.66
gY FSL								
A	0–3	0.46	0.007	5.35	0.84	0.084	0.021	2.12
B_1	4½–14	0.75	0.013	6.06	0.61	0.087	0.022	1.92
B_2	16½–29	0.63	0.011	7.44	0.82	0.087	0.027	2.62
B_3	32–43	2.85	0.010	8.57	0.46	0.082	0.032	3.94
yG FSL								
A	0–3	0.33	0.015	5.49	1.03	0.105	0.022	4.75
B_1	4½–7	0.90	0.020	4.12	0.39	0.063	0.018	3.93
B_2	10–25	0.69	0.011	4.59	0.31	0.064	0.016	2.23
B_3	27–36	0.68	0.009	5.61	0.27	0.052	0.018	5.12

Total phosphorus. The level of phosphorus reserve is higher in the crest soils than in the trough soils. And on the crest, the surface layers of the virgin soils contain more phosphorus than do those of the cultivated soils. This may be explained by the fact that phosphorus taken by agricultural crops is seldom returned to the soil, whereas the contrary is true of native grass cover. An eluviation-illuviation of phosphorus was observed in all the soils except yG FSL. Mattson *et al.* (6) found a similar course of translocation of the different forms of phosphorus in some podzolic soils of Sweden.

Total potassium. Since the total potassium content of the soils depends on the availability of potassium to plants, the degree of potassium saturation of the exchange complex, and the relative abundance of the potassium-bearing soil and clay minerals, it can hardly lead to any positive inference in pedogenic studies. Table 1, however, shows that, in the illuvial zone of the soils under investigation, potassium has been deposited.

DISTRUBITION OF IRON OXIDE

The different forms of iron oxide—free, combined, and total—in the colloid, noncolloid, and total fine-earth fractions of soil were determined. Results of the analyses are recorded in table 2.

The vertical distribution of free iron oxide in the total fine-earth fractions indicates unfailing illuviation of this oxide in the B horizons of all the soils—a feature that is clearly podzolic. In the noncolloid fractions also, the free iron oxide followed approximately the same course as in the total soil. It is noteworthy that in the B_2 horizons the level of free iron oxide in the noncolloid as well as in the total fine earth fractions is significantly lower in the trough soils (gY FSL and yG FSL) than in the crest soils, probably because of the utilization of free iron oxide in the formation of concretions in the subsoil horizons of the trough soils and as observed in the field (5).

The percentage concentration of free iron oxide in the colloid fraction was found to be higher in the illuvial zone, exhibiting a preferential enrichment in the B_1 horizons of bG FSL, gY YSL, and yG FSL. Again the percentage of free iron oxide in the colloid fractions shows an illuviation in the B horizons of all the soils except gY FSL. In bG FSL the degree of illuviation is limited to the area from the A_{1b} horizon to the B_1 horizon. These two findings indicate that iron oxide, since it is independent of clay, moved downward. That iron oxide can move independently in the ionic as well as in the colloidal form has also been shown by Deb (2), Karim[2], and others. Free iron oxide in the total fine-earth fraction showed a positive correlation with loss on acid treatment (table 3).

Combined iron oxide comprises the iron of the ferruginous minerals in soil and clay and also of the concretions too minute to be retained by a 2-mm. sieve. The ferruginous minerals, particularly in the clay fractions, may be iron-bearing clay minerals, such as goethite, hematite, or limonite, in the colloid fractions. Obviously in the soils under investigation the possibility of finding nontronite in the clay minerals is remote. The only alternative conditions which allows iron to remain in a combined state in the colloid fractions is the presence of adventitious iron minerals of different hydration, a condition which is quite likely to occur in the soils of tropical and subtropical climates.

The data on combined iron oxide indicate that this form of iron oxide showed relatively higher amounts of adventitious hydrated iron minerals in the surface horizon colloids and noncolloids. The surface horizons were those most subject to the tropical mineralization process, which liberated a considerable amount of iron

[2] Karim, A. 1951. Unpublished doctoral dissertation, Adelaide University, South Australia.

TABLE 2

Distribution of different forms of iron oxide in colloid and noncolloid fractions of Nanakhi soils

Soil Type and Horizon	Total Fe_2O_3 in Soil	Total Fe_2O_3 in Non-colloid	Total Fe_2O_3 in Colloid	Free Fe_2O_3 in Soil	Free Fe_2O_3 in Non-colloid	Free Fe_2O_3 in Colloid	Combined Fe_2O_3 in Soil	Combined Fe_2O_3 in Non-colloid	Combined Fe_2O_3 in Colloid	Concentration of Free Fe_2O_3 in Colloid
	%	%	%	%	%	%	%	%	%	%
bG FSL										
A_{1a}	4.96	3.57	10.53	2.52	1.60	6.68	2.44	1.97	3.85	50.20
A_{1b}	5.24	3.96	9.75	2.74	1.78	6.30	2.50	2.18	3.45	49.63
B_1	6.25	4.00	9.45	3.58	1.64	6.40	2.67	2.36	3.05	74.70
B_2	6.90	4.85	9.45	4.00	2.19	6.12	2.90	2.66	3.33	72.50
B_3	—	—	—	—	—	—	—	—	—	—
DG FSL										
A_{1a}	3.64	2.29	10.24	1.72	0.96	5.39	1.92	1.33	4.85	54.76
A_{1b}	4.61	3.51	10.75	2.03	1.39	5.57	2.58	2.12	5.18	42.29
B_1	5.33	2.25	9.68	3.13	1.39	5.61	2.20	0.86	4.07	67.54
B_2	—	—	—	—	—	—	—	—	—	—
B_3	5.69	2.69	9.22	3.37	1.97	5.12	2.32	0.72	4.10	69.21
G FSL/1										
A	3.62	2.89	8.47	1.59	1.15	4.53	2.03	1.74	3.94	37.11
B_1	3.99	2.50	8.56	2.03	1.01	5.17	1.96	1.49	3.39	62.56
B_2	6.45	2.73	10.55	3.83	2.33	5.49	2.62	0.40	5.06	69.79
B_3	—	—	—	—	—	—	—	—	—	—
G FSL/2										
A	4.13	3.02	9.01	2.08	1.47	4.71	2.05	1.55	4.30	43.14
B_1	4.81	3.00	9.01	2.22	2.11	4.74	2.59	0.89	4.27	65.74
B_2	6.10	2.91	9.54	3.40	2.00	4.90	2.70	0.91	4.64	71.39
B_3	—	—	—	—	—	—	—	—	—	—
gY FSL										
A	4.96	3.88	9.36	1.91	0.84	6.22	3.05	3.04	3.14	65.96
B_1	5.70	3.40	10.22	2.44	0.95	5.38	3.26	2.45	4.84	75.73
B_2	—	—	—	—	—	—	—	—	—	—
B_3	5.59	2.93	8.01	2.88	2.28	3.43	2.71	0.65	4.58	64.66
yG FSL										
A	3.94	1.91	10.90	1.76	0.74	5.30	2.18	1.17	5.60	69.19
B_1	3.99	1.57	11.40	2.17	0.49	7.31	1.82	1.08	4.09	84.11
B_2	4.06	1.87	9.90	2.13	0.99	5.20	1.93	0.88	4.70	66.82
B_3	—	—	—	—	—	—	—	—	—	—

oxide. The low pH values of the soils would probably allow free downward drainage of the liberated iron, but the A horizons of the soils under consideration, with their relatively greater oxidizing and hydrolyzing capacities, offer possibilities for the fixation of iron as adventitious minerals in the colloid and non-colloid fractions.

COMPOSITION OF CLAY FRACTION

The chemical analysis of clay determined the SiO_2–R_2O_3, SiO_2–Al_2O_3, and Al_2O_3–Fe_2O_3 ratios, with the results given in tables 3 and 4. The data show that: (*a*) the SiO_2–R_2O_3 ratio of approximately 2 varies little with depth in the profiles; (*b*) the SiO_2–Al_2O_3 ratio or Harrassowitz's (3) *ki*-value varies from 2 to 3 for all the soils under investigation, and seems to exhibit a fair constancy down the profile; (*c*) the Al_2O_3–Fe_2O_3 ratio varies between 3 and 4 and seems to be fairly constant throughout the profiles, which indicates that there has been no distinct

TABLE 3

*Fusion analyses of the clay fractions of Nanakhi soils**

Soil Type and Horizon	$\frac{SiO_2}{Al_2O_3 + Fe_2O_3}$	$\frac{SiO_2}{Al_2O_3}$	$\frac{Al_2O_3}{Fe_2O_3}$
bG FSL			
A_{1a}	2.02	2.57	3.61
A_{1b}	1.90	2.35	4.21
B_1	1.10	2.19	4.68
B_2	1.93	2.35	4.60
B_3	—	—	—
DG FSL			
A_{1a}	2.07	2.68	3.43
A_{1b}	1.84	2.51	2.70
B_1	2.23	2.84	3.61
B_2	—	—	—
B_3	1.92	2.33	4.69
G FSL/1			
A	2.12	2.59	4.52
B_1	2.00	2.47	4.81
B_2	1.96	2.45	4.04
B_3	—	—	—
G FSL/2			
A	2.06	2.52	4.50
B_1	2.16	2.65	4.39
B_2	1.96	2.39	4.52
B_3	—	—	—
gY FSL			
A	1.90	2.33	4.47
B_1	1.98	2.46	4.11
B_2	—	—	—
B_3	2.66	3.33	3.92
yG FSL			
A	1.92	2.50	3.33
B_1	2.01	2.60	3.38
B_2	2.01	2.39	3.57
B_3	—	—	—

* Ratios are expressed as gram-molar ratios on ignited clay

TABLE 4

Fusion analyses of clay fractions of Nanakhi soils

Soil Type and Horizon	SiO_2	Fe_2O_3	Al_2O_3
	%	%	%
bG FSL			
A_{1a}	36.74	10.53	24.26
A_{1b}	36.34	9.75	26.33
B_1	36.45	9.45	28.25
B_2	38.35	9.45	27.76
B_3	—	—	—
DG FSL			
A_{1a}	35.43	10.24	22.45
A_{1b}	27.53	10.75	18.57
B_1	37.28	9.68	22.30
B_2	—	—	—
B_3	37.91	9.22	27.60
G FSL/1			
A	37.20	8.47	24.46
B_1	37.30	8.56	26.31
B_2	39.12	10.55	27.18
B_3	—	—	—
G FSL/2			
A	38.40	9.01	25.89
B_1	39.32	9.01	25.26
B_2	38.69	9.54	27.54
B_3	—	—	—
gY FSL			
A	36.53	9.36	26.70
B_1	38.84	10.22	26.81
B_2	—	—	—
B_3	39.37	8.01	20.08
yG FSL			
A	34.05	10.90	23.16
B_1	37.71	11.40	24.61
B_2	36.26	9.90	22.45
B_3	—	—	—

preferential movement of Fe_2O_3 or Al_2O_3 with respect to each other; and (*d*) the high SiO_2–R_2O_3 ratios seem to conform to the total cation-exchange capacity of 13 to 28 me. per 100 g. (5), which indicates that the soils investigated represent a stage of development intermediate between that of highly siliceous soils and ferralitic soils.

FUSION ANALYSES OF FINE-EARTH FRACTIONS

The fine-earth fractions (<2 mm.) were analyzed for SiO_2, Fe_2O_3, and Al_2O_3 to determine the probable composition of the parent materials of the soils under

TABLE 5

*Fusion analyses of fine-earth fractions of Nanakhi soils**

Soil Type and Horizon	SiO_2	Fe_2O_3	Al_2O_3	SiO_2/R_2O_3†
	%	%	%	
bG FSL				
A_{1a}	71.56	4.96	6.89	12.18
A_{1b}	71.10	5.24	6.86	11.85
B_1	59.58	6.25	14.11	5.61
B_2	55.41	6.90	16.49	4.53
B_3	56.62	6.78	14.99	4.99
DG FSL				
A_{1a}	77.62	3.64	5.51	16.81
A_{1b}	78.62	4.61	3.43	21.13
B_1	64.10	5.33	12.77	6.75
B_2	59.43	5.64	17.21	4.83
B_3	62.06	5.69	15.83	5.41
G FSL/1				
A	76.62	3.62	4.95	17.99
B_1	71.34	3.99	9.71	9.91
B_2	59.95	6.45	15.99	4.91
B_3	58.31	6.55	15.99	4.91
G FSL/2				
A	77.12	4.13	5.49	16.06
B_1	75.04	4.81	6.29	13.75
B_2	60.85	6.10	14.72	5.56
B_3	53.98	6.13	20.68	3.75
gY FSL				
A	73.79	4.96	8.69	10.60
B_1	76.38	5.70	6.22	13.12
B_2	67.54	4.41	12.54	4.50
B_3	58.92	5.59	16.83	4.93
yG FSL				
A	73.19	3.94	7.45	12.33
B_1	74.38	3.99	7.45	12.69
B_2	73.74	4.06	8.53	11.38
B_3	65.29	5.65	10.41	7.94

* Fine-earth fractions <2 mm.

† Gram-molars ratios.

investigation [following Pendleton and Sharasuvana (7)]. The results of the analyses are given in table 5.

The data show that: (*a*) the SiO_2 content varies from about 50 to 70 per cent and decreases with depth; (*b*) the Fe_2O_3 content varies between about 3 and 6 per cent and rises with depth; (*c*) the Al_2O_3 content varies from about 6 to 20 per cent and rises with depth; and (*d*) the SiO_2–R_2O_3 ratio in the surface horizon varies from 10.60 to 21.13 and narrows to a minimum of 3.75 in the subsoils.

According to Pendleton and Sharasuvana (7) these findings indicate that the parent materials of the soils were probably of mixed origin, which suggests that the soil materials here were of a heterogeneous nature, a conclusion also inferred from geochemical considerations (5). The ratio of fine sand to coarse sand (5) further supported the suggested heterogeneity in parentage.

SOIL CLASSIFICATION

From the Plio-Pleistocene era weathering forces of a tropical climate have been responsible for an intense mineralization of the red argillaceous parent materials of heterogeneous composition which covered the floor of the sea of Tethys. Subsequently these weathering forces were instrumental in the removal of alkalies and alkaline earths from the seat of liberation to the ground water. At the same time the total soluble salts were gradually removed from the profile, lowering the pH to the acid side. Continued high temperature allowed organic matter little opportunity to accumulate.

Continuous high leaching of the soil has gone so far as to attack exchangeable cations and has brought about an ingress of H^+ in the exchange positions to an extent of approximately 50 per cent of the total cation-exchange capacity. As a result the destructive decompositions of clay colloids eventually lowered the SiO_2–R_2O_3 ratio to about 2, by which the presence of predominantly kaolinitic minerals is indicated. Leaching has also gone so far as to mobilize clay and to free sesquioxides from the A horizons, and thus to form in all soils light textured gray to grayish A horizons and heavy brown to red-brown B horizons, an evolutionary trend which indicates the climatogenic character of the soils.

The following essential morphological, textural, and physicochemical characteristics of these soils (5) and their chemical characteristics provide a key to their genetic classification:

(*a*) Gray to dark gray friable A horizon of fine sandy loam
(*b*) Brown to red-brown clayey B horizon of granular structure
(*c*) Presence of concretions in the B horizons of the trough soils
(*d*) Profiles completely leached of carbonates
(*e*) Reaction moderately acid (pH 4 to 6)
(*f*) Eluviation of free Fe_2O_3 from the A horizon and illuviation in the B horizon
(*g*) The colloidal complex fairly well supplied with exchangeable metal ions, that is, not highly base-unsaturated
(*h*) Higher percentage base saturation of the colloidal complex in the B horizon than in the A horizons
(*i*) SiO_2–R_2O_3 ratio of clay about 2
(*j*) SiO_2–Al_2O_3 ratio of clay approximately 2 to 3
(*k*) No differential movement of SiO_2 or R_2O_3 of clay; fairly constant SiO_2–R_2O_3 and SiO_2–Al_2O_3 ratios down the profiles

Clearly on the basis of these characteristics the soils can be classified as gray-brown podzolic (9). The climatic indexes also fully subscribe to such a classification (9). There is nothing strange about the presence of concretions in podzolic soils (1).

SUMMARY

The chemical characteristics of samples of various types of soils of the Nanakhi series in East Pakistan and of corresponding clay fractions of these soils are reported. On the basis of these results, in conjunction with earlier morphological and laboratory findings, the soils have been classified as gray-brown podzolic.

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CLAY MINERALS OF SOUTH AFRICAN SOIL GROUPS: IV. SOILS OF THE TEMPERATE REGIONS

C. R. VAN DER MERWE AND H. HEYSTEK

Union of South Africa Department of Agriculture and South African Council for Scientific and Industrial Research[1]

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The soil-forming factors under which the South African soil groups have developed, vary from desert to subtropical humid conditions with rainfall normals ranging from 2 to more than 48 inches. The predominant clay minerals (2, 3, 4) are hydrous micas in the desert and semiarid regions, montmorillonite in the subtropical black clays, and kaolinite in the lateritic red and yellow earths and in the gray and brown ferruginous lateritic soils.

The soils reviewed in this article have developed mainly from sedimentary rocks under temperate conditions and a relatively high rainfall. The morphological characteristics and essential relevant chemical data for the following soil groups and subgroups (1) are discussed: podzolic soils in (*a*) High Veld prairie soils, (*b*) semicoastal belt of the eastern Cape Province, (*c*) Natal coastal belt, and (*d*) southwestern and southern Cape Province; and subtropical brown forest soils in the Low Veld.

TECHNIQUES

The automatic differential thermal apparatus used for this investigation has been described in detail in another paper (6). The x-ray patterns in the x-ray diffraction investigation were obtained with a Philips high-angle spectrometer goniometer, type 42201/2, with CoKα radiation ($\lambda = 1.78890$ A.), and an automatically recording Brown Electronik strip-chart potentiometer.

RESULTS

The soil colloid fractions ($<2\mu$) representative of the various horizons of all the profiles of the soil groups in this investigation, which were described previously (1) in detail, were examined by x-ray diffraction and differential thermal methods. More than one clay mineral was present in most of the colloid fractions, and by differential thermal methods alone individual clay minerals and especially mixed-layer clay minerals could not be positively identified. There is no marked difference between the differential thermal analysis curve of the mixed-layer clay minerals and the type of curve obtained for numerous montmorillonoids. Since typical differential thermal curves and x-ray diffraction patterns of the various clay minerals were presented earlier (2, 3, 4), they have been omitted here.

[1] The senior author is with the Division of Chemical Services, Department of Agriculture, and the junior author with the National Chemical Research Laboratory, South African Council for Scientific and Industrial Research, Pretoria.

Podzolic soils

This soil group covers an enormous area, stretching from southcentral Transvaal through the eastern Orange Free State into the eastern Cape Province as far as the Great Fish River and thence along the east coast to the Tugela River in Natal. The soils are chemically and genetically related, but their differing morphology provides the basis for the division of the region into three subgroups.

High Veld prairie soils. This subgroup comprises the major part of the podzolic soil group and occurs in Transvaal, northeastern Free State, and the foothills of Basutoland. The elevation of the region is 5000 to 6000 feet above sea level, with a gently undulating surface relief in the open country and rolling to hilly in the vicinity of the mountains. Surface drainage is good.

Geologically the area consists almost entirely of sedimentary rocks—Ecca and Beaufort series (with dolerite intrusions) and Cave sandstone beds (7). The whole area is covered with grass consisting of *Hyparrhenia hirta*, *Themeda triandra*, and species of the genera *Cymbopogon* and *Andropogon*.

Climatically this region is classified by Köppen (5) as "warm temperate rainy" (Cwb) and by Thornthwaite as in the "sub-humid warm class" (CB′d) with dry winters. The average annual rainfall varies from 22 to more than 32 inches and decreases from east to west. Precipitation occurs in thunderstorms and heavy showers. Winter nights are cold; frost is severe; and snow very rare.

These soils are mainly residual and generally mature with well-developed horizons. Their internal drainage is impeded by claypan in the substrata. A general profile is as follows:

Horizon A_1: Dark grayish brown, friable to crumbly sandy loam; low humus content; abundant roots; 6 to 10 inches.

Horizon A_2: Yellowish brown, fairly open, crumbly sandy loam; few iron oxide concretions; abundant roots; deficient in organic matter; 6 to 12 inches.

Horizon B_1: Brownish yellow sandy loam; slightly compact but crumbly; fair amount of iron oxide concretions; roots irregular and few; 3 to 15 inches.

Horizon B_2 or G_1: Dark bluish gray, speckled brownish and reddish yellow clay; fairly to very compact; when wet, plastic and rather impervious, and when dry, column-like; few roots confined to fissures; 15 to 28 inches. This horizon is sometimes subdivided into B_3 or G_2.

Horizon C: Light gray clay; compact and cloddy; partly decomposed rock which when moist is tough and plastic; 6 to 14 inches.

Mechanical analysis (table 1) of these soils is very similar with a relatively low clay content in the A and a marked increase in the B horizons. The colloid fractions of the soils, derived from the Cave sandstone, are considerably less than those derived from the Beaufort series.

Chemical composition of the colloids from the various horizons of the profiles follows a regular trend, that is, SiO_2 decreases and Al_2O_3 increases gradually with depth. Fe_2O_3 is low but shows a marked increase in the B_1 horizon. K_2O content of the colloids is high and fairly constant.

Molecular SiO_2–R_2O_3 and SiO_2–Al_2O_3 ratios of the clay fractions vary with depth from high to fairly low. When these profiles were sampled, the undecom-

TABLE 1

Analytical and derived data for High Veld prairie soils

Profile, Geology, Rainfall, Sample No.	Horizon	Depth	Clay <0.002 mm.	Analysis of Oven-Dried Colloid					
				SiO_2	Fe_2O_3	Al_2O_3	K_2O	$\frac{SiO_2}{R_2O_3}$	$\frac{SiO_2}{Al_2O_3}$
		in.	%	%	%	%	%		
Senekal: Beaufort beds; 24 in. a year									
A 2871	A_1	0–8	16.6	65.5	4.4	23.7	2.69	4.17	4.68
A 2872	A_2	8–14	19.4	61.9	4.6	26.8	2.61	3.52	3.91
A 2873	B_1	14–24	31.9	56.7	8.6	29.2	2.44	2.77	3.29
A 2874	B_2 or G	24–52	69.0	52.5	7.9	35.2	2.32	2.21	2.52
A 2875	C	52–66	75.9	52.1	8.1	35.9	2.32	2.14	2.46
Winburg: Beaufort beds; 20 in. a year									
A 2876	A	0–10	13.1	52.6	9.4	31.0	2.78	2.41	2.87
A 2878	B_2 or G	25–40	59.3	53.4	9.0	31.4	2.08	2.44	2.88
A 2879	C	40–48	50.9	54.5	9.2	30.7	2.13	2.52	3.01
Thaba 'Nchu: cave sandstone; 24 in. a year									
A 2819	A_2	6–12	17.1	61.3	3.6	28.5	2.68	3.37	3.65
A 2821	B_1 or G_1	20–23	64.5	53.2	9.5	32.5	2.81	2.33	2.77
A 2823	B_3 or G_3	28–40	68.2	53.9	6.7	33.8	2.91	2.39	2.70
A 2824	C	40–46	61.4	53.6	7.6	32.9	2.95	2.41	2.76
Bethlehem: cave sandstone; 27 in. a year									
B 1008	A_1	0–10	13.2	52.1	9.9	31.4	2.34	2.34	2.81
B 1009	A_2	10–19	20.0	49.5	9.7	35.0	1.97	2.04	2.40
B 1010	B_1	19–30	26.3	48.2	10.3	35.6	2.06	1.91	2.29
B 1012	B_3 or G	38–50	48.1	50.1	9.1	34.8	2.54	2.09	2.44
Ararat (Harri-smith): cave sand-stone; 35 in. a year									
B 1013	A_1	0–18	15.2	59.9	7.6	35.2	1.86	2.53	2.88
B 1014	A_2	18–26	19.1	51.2	8.2	36.1	1.73	2.10	2.41
B 1015	B_1	26–34	22.7	51.9	8.2	35.7	1.85	2.15	2.46
B 1016	B_2 or G	34–50	46.6	52.5	5.5	36.3	2.32	2.23	2.45
Cala: cave sand-stone; 24 in. a year									
B 1629	A_1	0–9	13.0	68.6	4.7	20.9	1.76	4.86	5.55
B 1630	A_2	9–14	12.0	69.5	3.9	21.6	1.83	4.89	5.45
B 1632	B	19–28	42.4	58.7	6.6	28.1	2.00	3.07	3.53
B 1633	C	28–40	35.4	57.2	9.1	27.7	1.69	2.89	3.53

posed parent material unfortunately was not taken. This is a serious omission in soils derived from sedimentary rocks, because it prevents obtaining a clear picture of the weathering of parent rock to soil. The relatively low ratios in the B and C horizons seem to indicate presence of clay minerals of the kaolinite group.

The clay mineral composition of the colloid fractions from the different soil

TABLE 2

X-ray results for High Veld prairie soils

Profile and Sample No.	Clay Mineral Composition
Senekal	
A 2871	Soil kaolin, montmorillonite
A 2872	Soil kaolin, illite
A 2873	Illite, soil kaolin
A 2874	Illite, soil kaolin
A 2875	Illite-montmorillonoid mixed-layer, soil kaolin
Winburg	
A 2876	Illite, soil kaolin
A 2878	Illite-montmorillonoid mixed-layer, soil kaolin
A 2879	Soil kaolin, little illite-montmorillonoid, mixed-layer.
Thaba 'Nchu	
A 2819	Illite, soil kaolin
A 2821	Illite, soil kaolin
A 2823	Illite-montmorillonoid mixed-layer, little soil kaolin
A 2824	Illite-montmorillonoid mixed-layer, little soil kaolin
Bethlehem	
B 1008	Soil kaolin, illite
B 1009	Soil kaolin, illite
B 1010	Illite and soil kaolin
B 1012	Illite and very little soil kaolin
Ararat	
B 1013	Kaolinite*, illite-montmorillonoid mixed-layer
B 1014	Kaolinite*, illite-montmorillonoid mixed-layer
B 1015	Kaolinite*, illite-montmorillonoid mixed-layer
B 1016	Illite-montmorillonoid mixed-layer, kaolinite*
Cala	
B 1629	Illite-montmorillonoid mixed-layer
B 1630	Illite-montmorillonoid mixed-layer, soil kaolin
B 1632	Illite-montmorillonoid mixed-layer, soil kaolin
B 1633	Illite-montmorillonoid mixed-layer, soil kaolin

* X-ray diffraction pattern indicates a kaolin mineral of a higher crystallinity than for the other soils investigated and referred to as soil kaolin.

profiles is summarized in table 2, where in column 2 the various clay minerals are reported in quantitative sequence.

Clay minerals in the various profiles are not what would be expected from the molecular SiO_2–R_2O_3 ratios; the B, G, and C horizons, for example, have relatively low ratios, but the predominant clay minerals are illite and illite-montmorillonoid mixed-layer minerals. In the A_1 horizons, again with high molecular ratios, soil kaolin predominates; colloidal silica is probably responsible for these high ratios.

Although no undecomposed parent rock samples were available for comparison, the first products of weathering did contain illite or illite-montmorillonoid mixed-layer clay minerals with little or no soil kaolin present. The ratio of soil kaolin to other clay minerals increases through the upper B and A horizons and actually

becomes the predominant mineral in the topsoil of the Senekal, Bethlehem, and Ararat profiles. Illite-montmorillonoid mixed-layer clay minerals occur in the surface horizon only in the Cala and Ararat profiles.

Soils derived from dolerite intrusive into sedimentary rocks are all black clays with montmorillonite as the predominant clay mineral (High Veld intrazonal black clay) (3).

Soils of semicoastal belt of eastern Cape Province. This subgroup of the podzolic soils comprises a rectangular tract of country along the east coast of the Cape Province; it extends from the Great Fish River for some distance into Natal and westward to Cathcart and King Williams Town.

The surface relief of the region is fairly regular and undulating to steep rolling; the area is dissected by numerous water courses which serve as drainage channels. The Ecca and Beaufort beds, (7) with extensive dolerite intrusions in some localities, constitute its geology. Vegetation consists almost entirely of the tall grass species.

Climate is classified according to Köppen (5) as "humid temperate" (Cfwb) and by Thornthwaite as in the "sub-humid warm class" (CB′d). Annual rainfall ranges from 23 to 32 inches and decreases from east to west. Precipitation occurs mainly during summer in thunderstorms and in heavy downpours. Winters are dry with some light frost, and summers are hot.

These soils are mainly residual, but they are evidently influenced to some degree by colluvial wash from the slopes of the rolling ridges. Although the profiles are generally very shallow, the soils are well developed and the horizons well defined, particularly in the eastern area. Representative profiles of the western and eastern areas are given, as follows, under Cathcart and Butterworth, respectively.

Cathcart profile

Horizon A_1: Dark gray sand; friable, breaking up into soft crumbs; abundant thin roots; 8 inches.

Horizon A_2: Light grayish brown sand but otherwise similar to A_1; 7 inches.

Horizon B_1: Light gray, crumbly loamy sand with gravel, which consists mainly of ferruginous concretions; 4 inches.

Horizon B_2 or G: Brown, mottled light brown, fairly hard, sandy clay with occasional sandstone fragments; compact, vertically fissured—cracks filled with bluish gray colloidal material; 3 inches.

Horizon C: Partly decomposed rock.

Butterworth profile

Horizon A: Bluish gray, crumbly sandy loam full of holes and burrows (earthworms and moles); abundant roots; humus poor; 10 inches.

Horizon B: Dark brown, gravelly sandy clay loam—gravel consists of well-packed but uncemented "buckshot" ferruginous concretions; fairly hard; 12 inches.

Horizon C: Dark brown, mottled yellowish brown, with streaks colored light bluish gray, partly decomposed, fairly hard shale; 8 inches.

The clay content of the profiles (table 3) indicates differentiation of the soil material into horizons, but not to the degree evident in the High Veld prairie

TABLE 3

Analytical and derived data for semicoastal belt soils

Profile, Geology, Rainfall, Sample No.	Horizon	Depth	Clay <0.002 mm.	Analysis of Oven-Dried Colloid					
				SiO_2	Fe_2O_3	Al_2O_3	K_2O	$\frac{SiO_2}{R_2O_3}$	$\frac{SiO_2}{Al_2O_3}$
		in.	%	%	%	%	%		
Cathcart: Beaufort beds; 25 in. a year									
B 1603	A_1	0–5	9.2	66.5	4.8	20.7	3.39	4.76	5.46
B 1604	A_2	5–12	9.8	67.0	5.0	20.5	3.33	4.82	5.56
B 1605	B_1	12–16	12.7	63.6	5.3	23.3	3.23	4.06	4.65
B 1606	B_2 or G	16–19	26.8	53.5	5.1	33.6	3.32	2.47	2.70
Butterworth: Beaufort beds; 27 in. a year									
B 1617	A	0–10	21.6	75.3	4.0	14.8	2.25	7.39	8.69
B 1618	B	10–22	27.6	64.9	8.1	20.4	2.44	4.32	5.40
B 1619	C (rock)	22+							

soils. The steep topography promotes lateral removal of colloidal materials from the soil section.

The chemical composition of the colloids shows a gradual decrease of SiO_2 and an increase of Al_2O_3 with depth. Fe_2O_3 is fairly constant except for sample B 1618. Fe_2O_3 contents of the colloid fractions do not emphasize the morphological characteristics, because the Fe_2O_3 occurs mainly in concretions. In the total soil analysis of the Butterworth profile, the percentages of Fe_2O_3 are 3, 14, and 5 for the A, B, and C horizons, respectively. The K_2O content of the colloids is high and fairly constant.

High molecular SiO_2–R_2O_3 and SiO_2–Al_2O_3 ratios, particularly in the A and B horizons, and high K_2O content indicate the presence of hydrous mica clay minerals in these soils. The ratios of sample B 1606 are related to those of the High Veld prairie soils.

In the clay minerals of the Cathcart profile (table 4) illite predominates in practically all the horizons. Very little alteration of the clay minerals appears to have occurred.

In the Butterworth profile the inherited clay minerals of the parent rock (B 1619)—illite and some soil kaolin—appear in the solum with the disappearance of montmorillonite.

In contrast to the black clays, which are derived from dolerite in the High Veld prairie soils and which have only montmorillonite as clay mineral, the clay mineral of those developed from a similar rock in this subgroup is soil kaolin even in the C horizon (3).

Soils of the coastal belt of Natal. This podzolic subgroup is an extension northeastward of the subgroup of the semicoastal belt of eastern Cape Province and is confined to a narrow strip along the coast terminating north of Empangeni

TABLE 4

X-ray results for semicoastal belt soils

Profile and Sample No.	Clay Mineral Composition
Cathcart	
B 1603	Illite-montmorillonoid interlayered
B 1604	Illite, trace of soil kaolin
B 1605	Illite, soil kaolin
B 1606	Illite, soil kaolin
Butterworth	
B 1617	Illite, soil kaolin, very weak x-ray pattern
B 1618	Illite, soil kaolin, very weak x-ray pattern
B 1619	Illite, montmorillonite, trace of soil kaolin

in Natal. The topography of the country is irregular and the terrain intersected by numerous rivers. There is a steep rise in altitude from the sea inland. Surface relief, which is steep undulating to rolling, is not conducive to formation of well-developed mature soils.

The main portion of this subgroup has been developed for sugar cane. Indigenous vegetation consists of dense bush and grass. The geological formation, which consists of Table Mountain sandstone, Ecca and Dwyka series, with dolerite intrusions and granite (7), occurs in narrow strips parallel to the coast.

Köppen and Thornthwaite (5) classify the climate of this region, respectively, as "humid temperate" (Cfwa) and "sub-humid warm" (CB′r). Annual rainfall varies from 40 to 65 inches and occurs during the hot summers; winters are relatively dry and mild.

The soils are generally immature, with profiles ranging in depth from several inches to several feet, and with ferruginous accumulation varying from impregnation of porous shale fragments to a well-defined horizon of "pea ore" concretions. The well-developed profile is as follows:

Horizon A_1: Dark grayish brown, crumbly sandy loam; humus in fair quantity and roots abundant; 6 to 8 inches.

Horizon A_2: Dark grayish brown sandy clay loam, but otherwise, except for deficient humus, similar to horizon A_1; 6 to 8 inches.

Horizon B_1: Blackish brown, well-packed but uncemented "pea ore" iron oxide concretions mixed with little sandy clay loam; 3 to 4 inches.

Horizon B_2 or G: Yellowish brown, mottled bluish gray cloddy clay; walls of the vertical fissures are colored dark brown by infiltrated colloidal material; 10 to 14 inches.

Horizon C: Yellowish brown, mottled blue-gray, partly decomposed horizontally bedded shale, which becomes gradually harder with depth.

Parent Rock: Yellowish brown, hard, horizontally bedded shale.

The colloid fractions (table 5) indicate eluviation of the finer particles from the A horizons by lateral erosion and illuviation into the B horizons as evidenced by colloidal material on the walls of cracks. The horizon of accumulation is responsible for the temporary waterlogged conditions essential to ferruginous formation.

TABLE 5

Analytical and derived data for soils of Natal coastal belt

Profile, Geology, Rainfall, Sample No.	Horizon	Depth	Clay <0 002 mm.	Analysis of Oven-Dried Colloid					
				SiO_2	Fe_2O_3	Al_2O_3	K_2O	$\frac{SiO_2}{R_2O_3}$	$\frac{SiO_2}{Al_2O_3}$
		in.	%	%	%	%	%		
Mt. Edgecombe Ecca Series; 40 in. a year									
B 1957A	A_2	6–12	17.7	59.3	10.2	24.3	0.78	5 03	6.38
B 1959	B_2 or G	16–30	52.7	54.3	11.0	27.6	2.17	2.67	3.34
B 1960	C	30–44	23.4	58.2	7.9	26.4	2.60	3.14	3.74
B 1961	Shale								
Darnall Dwyka tillite; 45 in. a year									
B 3204	A_2	8–16	17.6	57.9	9.5	24.1	2.03	3.25	4.06
B 3206	B_2 or G	20–30	43.2	47.5	14.5	30.9	1.50	2.00	2.60
B 3207	C	30–42	21.0	53.2	11.8	26.4	2.36	2.65	3.41

The chemical composition of the colloids shows a marked regularity of SiO_2 and R_2O_3, the former decreasing from the A to the B horizons and thereafter increasing again, whereas for the latter, the reverse is true. The K_2O content of the colloids is generally fairly high, particularly in the C horizon.

Molecular SiO_2–R_2O_3 and SiO_2–Al_2O_3 ratios of the clay fractions are fairly high to high, which indicates montmorillonitic and hydrous mica clay minerals. They decrease from the A to the B horizons and thereafter increase again.

The undecomposed shale (B 1961, Mt. Edgecombe) contains only an illite-montmorillonoid mixed-layer clay mineral. As the first products of weathering, horizon C and also B_2 contain illite and soil kaolin as clay minerals, and the A horizon only soil kaolin.

In the Darnall profile, derived from Dwyka tillite, the C horizon (B 3207) contains soil kaolin, illite, and montmorillonite as clay minerals. These minerals persist in the B_2 horizon, but in the A_2 horizon only soil kaolin is found.

Southwestern and southern Cape Province soils: (a) grayish brown to dark brown soils. Narrow strips of these soils are found south and east of Tulbagh to the coast and in George. Two wide tracts of this soil exist also east of George along the coast to Port Elizabeth and north of Tulbagh slightly inland.

The surface relief of the country varies from gently undulating to mountainous. Drainage is excessive and there are numerous fresh water springs.

Table Mountain sandstone (7) constitutes the geological formation of the country. In the valleys shales are found in limited areas. Vegetation consists of bush and sour grasses on plateaus and gentle slopes. In the vicinity of Knysna, temperate evergreen forests occur.

The climate, influenced by mountain ranges, is complicated. Rainfall in the southwestern Cape Province occurs during the winter months and ranges from

TABLE 6

X-ray results for soils of Natal coastal belt

Profile and Sample No.	Clay Mineral Composition
Mt. Edgecombe	
B 1957A	Soil kaolin
B 1959	Illite, soil kaolin
B 1960	Illite, soil kaolin
B 1961	Illite-montmorillonoid interlayered
Darnall	
B 3204	Soil kaolin
B 3206	Soil kaolin, illite, some montmorillonite
B 3207	Soil kaolin, illite, some montmorillonite

17 inches in the north to 100 inches between Ceres and Somerset West. Rainfall of the eastern extension ranges from 15 to 45 inches a year with year-round distribution. The mountains have mild summers and cold winters; some peaks have snow for long periods.

Because of the mountainous terrain, the soils, mainly derived from Table Mountain sandstone, are poorly developed. There is no soil on the mountain tops, but where the surface relief on the slopes is favorable, soils occur in various stages of formation. The immature soils are mixed to some degree with rock debris. A typical profile of the deeper, mature soils of colluvial origin, on the level and undulating ground under a plantation of pines, is described as follows:

Concordia profile

Horizon A_1: Very dark brown sandy loam; friable to loose; abundant organic matter and roots; 6 inches.

Horizon A_2: Light brown, friable sandy loam; deficient in humus but with abundant roots; 11 inches.

Horizon A_3: Fairly similar to horizon A_2 but with fewer roots; 19 inches.

Horizon B_1: Light reddish brown, crumbly sandy loam; root content medium; 19 inches.

Horizon B_2: Reddish brown, mottled black, crumbly sandy loam; 12 inches.

Horizon B_3: Similar to horizon B_2; 12 inches.

Horizon C: Decomposing rock.

In some valleys hemmed in by Table Mountain sandstone, the soils under pine plantations and derived from Bokkeveld shale are of residual and residual-colluvial origin.

Witelsbos profile

Horizon A: Brown, changing gradually to yellowish brown, soft, crumbly clay; humus moderate; abundant roots; 6 inches.

Horizon B_1: Yellow clay, fairly dense and slightly plastic; medium roots; 12 inches.

Horizon B_2: Fairly similar to B_1, but less dense and with fewer roots; 12 inches.

Horizon C: Well-weathered pink shale; crumbly and soft; 6 inches.

These soils, as a result of the plantations, are better supplied with organic material than are normal virgin soils. The A_0 horizon of each profile has a 2-inch layer of fresh, dry, pine needles underlain by a 1-inch mulch and is dark brown.

TABLE 7

Analytical and derived data for soils of southern and southwestern Cape Province

Profile, Geology, Rainfall, Sample No.	Horizon	Depth	Clay <0.002 mm.	Analysis of Oven-Dried Colloid					
				SiO_2	Fe_2O_3	Al_2O_3	K_2O	$\frac{SiO_2}{R_2O_3}$	$\frac{SiO_2}{Al_2O_3}$
		in.	%	%	%	%	%		
Witelsbos: Bokkeveld shale; 45 in. a year									
A 7971	A	3–9	37.4	48.4	8.3	35.0	4.66	2.04	2.34
A 7972	B_1	9–21	42.1	46.7	9.0	35.8	4.32	1.90	2.21
A 7974	C	33–39	9.4	48.3	6.8	37.3	4.52	1.96	2.19
Concordia: Table Mountain sandstone; 40 in. a year									
A 8006	A_2	9–20	8.4	67.1	6.0	22.8	0.74	4.28	5.01
A 8007	A_3	20–39	10.8	59.6	7.0	28.0	0.98	3.05	3.54
A 8009	B_2	51–63	16.8	49.4	5.2	41.2	1.33	1.88	2.02

The physical composition of the two profiles (table 7) varies considerably, being influenced by the parent rock. In both profiles a certain amount of eluviation of the colloids from the A to the B horizon has taken place.

The potash content of the Witelsbos is very high and fairly constant throughout the profile, whereas that of the Concordia is medium to low and increases with depth.

Molecular SiO_2–R_2O_3 and SiO_2–Al_2O_3 ratios of the colloids of the Witelsbos profile are fairly low and constant, but those of the Concordia profile show marked decreases with depth.

Clay minerals of the Witelsbos profile are kaolinite and sericite throughout the profile, and most likely these were also the predominant clay minerals in the parent material (Bokkeveld shale, sample A 9522, table 9). Clay minerals in the A and B horizons of the Concordia profile are soil kaolin and montmorillonite, the latter decreasing slightly with depth. This is in accord with the molecular ratios of the clay fractions.

TABLE 8

X-ray results for soils of southern and southwestern Cape Province

Profile and Sample No.	Clay Mineral Composition
Witelsbos	
A 7971	Kaolinite, sericite
A 7972	Kaolinite, sericite
A 7974	Kaolinite, sericite
Concordia	
A 8006	Soil kaolin, montmorillonite
A 8007	Soil kaolin, montmorillonite
A 8009	Soil kaolin, little montmorillonite

TABLE 9

Analytical and derived data for soils of southwestern Cape Province

Profile, Geology, Rainfall, Sample No.*	Horizon	Depth	Clay <0.002 mm	Analysis of Oven-Dried Colloid					
				SiO_2	Fe_2O_3	Al_2O_3	K_2O	$\frac{SiO_2}{R_2O_3}$	$\frac{SiO_2}{Al_2O_3}$
		in.	%	%	%	%	%		
Caledon: Bokkeveld shale; 14 in. a year									
A 9519	A–B_1	0–13	22.2	44.9	18.7	28.7	4.23	1.87	2.66
A 9520	B_2	13–25	43.1	45.8	12.8	33.8	3.82	1.85	2.29
A 9521	C_1	25–31	43.9	48.0	12.6	32.5	3.50	2.01	2.51
A 9522	C_2	31–41	—	51.8	11.6	28.1	3.25	2.47	3.12

* X-ray results show following clay mineral composition: A 9519 and A 9520, kaolinite, sericite; A9521, kaolinite, sericite, illite-montmorillonoid mixed-layer; A9522, kaolinite, sericite, montmorillonite.

Southwestern and southern Cape Province soils: (*b*) *gravelly sandy clay loams.* These soils occur in low-lying plains in southwestern Cape Province. The two main bodies are found in the Malmesbury and the Caledon districts in broad open valleys which are in sharp contrast to the adjoining mountainous country noted under (*a*). Surface relief is undulating to gently rolling and the area is well drained by numerous, normally dry tributaries of the perennial rivers.

The geological formation of the Malmesbury area consists of Malmesbury shale, and that of the Caledon area of Bokkeveld shale (7). The plains, originally covered by bush and scrub (*Euryops tenuissimus*, *Eriocephalus umbellulatus*, and *Elytropappus rhinocerotis*), are now mainly used for wheat production.

The climate (5) is "warm with dry summers (Mediterranean)" (Csa, Csb) according to Köppen's classification, and "sub-humid warm" (CB′d, CB′r) and "semi-arid warm" (DB′d) according to Thornthwaite. Precipitation takes place during winter and ranges from 13 to 26 inches. Summers are hot and dry.

The Caledon profile which follows can be considered representative of these soils:

Caledon profile

Horizon A–B_1: Grayish brown, crumbly gravelly sandy loam, the gravel consisting of ferruginous concretions mixed with quartz grit and small angular shale fragments; as a result of cultivation the A horizon has been mixed with material from the B horizon; deficient in humus; 13 inches.

Horizon B_2: Reddish brown gravelly clay crumbly when dry and compact when wet; stones and gravel consist of hard and soft shale fragments; 10 inches.

Horizon C_1: Yellowish brown, mottled reddish brown, partly decomposed, rather soft shale containing an appreciable amount of clay; 6 inches.

Horizon C_2: Slightly weathered, grayish brown shale (Bokkeveld).

The clay content of the Caldon profile (table 9) is high in the B_2 and C horizons but rather low in the A-B_1 horizon, which has lost an appreciable amount of clay apparently through lateral eluviation.

The chemical composition of the soil shows a fairly high Fe_2O_3 content which

decreases with depth, and ad increasing SiO_2 content with depth. The Al_2O_3 and K_2O are high and fairly constant with maximums in the B_2 and A-B_1 horizons, respectively.

Molecular SiO_2–R_2O_3 ratios of the colloids are low and fairly constant, except for a sharp rise in the C_2 horizon. The SiO_2–Al_2O_3 ratios are medium with a sharp drop in the B_2 horizons and a rise in the C_2.

The clay mineral composition of the soil consists of kaolinite and sericite throughout the profile; in addition there are illite-montmorillonoid mixed-layer minerals in the C_1 horizon and montmorillonite in the C_2. Clay minerals of both this profile and the Witelsbos profile are derived from similar parent material and are thus related.

Subtropical brown forest soils (Low Veld)

These soils occur in a low-lying tract of country hemmed in by mountains along the northeastern border of the Union. The elevation above sea level is between 600 and 2500 feet and the surface relief consists of gently undulating ridges. The terrain is well drained by perennial rivers and their tributaries.

Granite, gneiss, and relatively small areas of basic igneous and sedimentary rocks (7) constitute the geology of the country. This region, called Low Veld, is well covered by a dense growth of trees, shrubs, and grass.

The climate of the Low Veld is "steppe" (BShw) according to Köppen's system and "semi-arid warm" (DB′d) according to Thornthwaite's (5). The rainfall, which ranges from 12 to 26 inches a year, occurs in summer. Winters are dry and mild.

The soils are residual and generally shallow. Morphological features of the well-developed soils of this group, influenced in each case by the parent material, vary considerably. The following profile descriptions indicate some of the variations:

Messina profile (granite-gneiss and overburden)

Horizon I: Brown with reddish tint, crumbly light sandy loam; deficient in humus; roots medium in quantity; 6 inches.

Horizon II: Reddish brown, slightly dense, crumbly sandy loam, quartz particles in fair quantity; 9 inches.

Horizon III: Reddish brown, crumbly stony sandy loam; abundant quartz particles and rock pebbles; 12 inches.

Horizon IV: Gravelly partly decomposed gneiss; 12 inches.

Horizon V: Yellowish brown fine gravelly sand; 6 or more inches.

Lebombo Flats profile (basalt)

Horizon I: Reddish brown, crumbly clay; roots medium in quantity; organic matter deficient; 10 inches.

Horizon II: Reddish brown, fairly dense, crumbly clay; 14 inches.

Horizon III: Light reddish brown changing to yellowish brown, fairly dense clay; 22 inches.

Horizon IV: Yellowish brown, crumbly to fairly dense coarse sandy loam; 14 inches.

Horizon V: Partly weathered rock; 12 inches.

Mkuzi Falls profile (dolerite)

Horizon I: Dark reddish brown, crumbly clay; humus poor; abundant roots; 10 inches.
Horizon II: Brownish red, crumbly clay; roots in fair quantity; 14 inches.
Horizon III: Dark brownish red clay; crumbly; occasional boulders which with depth increase in number; 12 inches.
Horizon IV: Dark brownish red, mottled black clay; crumbly to fine nutty; 36 inches.
Horizon V: Color, texture and structure as in IV; 12 inches.

Malopene profile (greenstone, talc, and chloritic schists)

Horizon I: Light reddish brown, crumbly sandy clay loam; deficient in humus; abundant roots; 6 inches.
Horizon II: Reddish brown, crumbly sandy clay loam; abundant roots; 18 inches.
Horizon III: Reddish brown well-weathered rock; crumbly but fairly dense; 12 inches (below this layer lies partly decomposed rock).

The clay contents of the brown forest soils (table 10) vary considerably from profile to profile, because of parent materials which dominate and characterize the mechanical composition of the soils. The soils developed from basic igneous rocks have high clay contents, but coarse fractions predominate in soils derived from acid igneous rocks.

Throughout the individual profiles derived from acid or basic igneous rocks, chemical analysis reveals a marked uniformity in the composition of the colloid

TABLE 10

Analytical and derived data for brown forest soils

Profile, Geology, Rainfall, Sample No.	Horizon	Depth	Clay <0.002 mm.	Analysis of Oven-Dried Colloid					
				SiO_2	Fe_2O_3	Al_2O_3	K_2O	$\frac{SiO_2}{R_2O_3}$	$\frac{SiO_2}{Al_2O_3}$
		in.	%	%	%	%	%		
Messina: granite-gneiss; 12 in. a year									
B 20	I	0–6	11.0	48.0	14.5	28.3	2.27	2.17	2.88
B 22	III	15–27	17.2	48.4	15.0	29.2	1.71	2.13	2.82
B 24	V	39–45	6.0	50.1	15.3	23.2	1.65	2.57	3.66
Lebombo Flats: basalt; 25 in. a year									
A 8149	I	0–10	43.0	45.9	18.4	27.6	1.14	1.98	2.82
A 8150	II	10–24	52.9	46.3	16.4	30.1	0.91	1.93	2.60
A 8151/2	III	24–46	32.7	48.0	17.1	27.4	0.69	2.12	2.97
A 8154	V	60–72	11.7	51.2	18.4	23.6	0.76	2.45	3.67
Mkuzi Falls: dolerite; 20 in. a year									
A 4901	III	24–36	63.9	46.7	12.9	35.7	1.51	1.80	2.21
A 4905	V	72–84	48.6	49.0	13.43	29.9	1.59	2.15	2.78
Malopene: basic rocks; 18 in. a year									
B 3164	I	0–6	28.9	44.8	19.5	26.7	1.88	1.94	2.85
B 3165	II	6–24	28.5	44.2	19.6	29.2	1.49	1.75	2.47
B 3166	III	24–36	40.3	44.2	19.9	28.6	1.57	1.81	2.62

TABLE 11

X-ray results for brown forest soils

Profile and Sample No.	Clay Mineral Composition
Messina	
B 20	Illite, some soil kaolin
B 22	Illite, some soil kaolin, montmorillonite
B 24	Montmorillonite, illite, some soil kaoline
Lebombo Flats	
A 8149	Soil kaolin, traces of illite and montmorillonite
A 8150	Soil kaolin
A 8151/2	Montmorillonite, soil kaolin
A 8154	Montmorillonite, soil kaolin
Mkuzi Falls	
A 4901	Soil kaolin
A 4905	Soil kaolin, trace of montmorillonite
Malopene	
B 3164	Illite, soil kaolin, some talc
B 3165	Illite, talc, soil kaolin, montmorillonite
B 3166	Talc, some soil kaolin, montmorillonite

fractions. The SiO_2, Fe_2O_3, and Al_2O_3 percentages are all fairly high and constant with only a gradual increase of SiO_2 and Fe_2O_3 with depth; Al_2O_3 shows a slight increase in horizon II but thereafter a decrease. K_2O content is medium in all the profiles except Lebombo Flats, where it is low.

Molecular SiO_2–R_2O_3 ratios of the soils are low, and the SiO_2–Al_2O_3 ratios moderate, but both these ratios increase from horizon II downward.

The clay mineral composition (table 11) of the surface layers seems to have been influenced by rainfall. Illite predominates in the lower (Messina and Malopene) and soil kaolin in the higher rainfall areas (Lebombo Flats and Mkuzi Falls). Montmorillonite is the predominant clay mineral of the decomposing gneiss and basalt of the Messina and Lebombo Flats profiles, respectively; illite and soil kaolin also are present.

CONCLUSIONS

Morphologically the two soil groups and their subgroups differ entirely from each other and justify separate classification. Except for a section of the brown forest soils, they have all developed under a rainfall sufficiently high to produce effective leaching and differentiation into well-defined horizons. They can be considered mature soils. Except the brown forest soils, they are derived from sedimentary rocks—sandstones or shales or both. These soil groups occur in a summer rainfall region with the exception of the southwestern Cape Province, which has a winter rainfall. Because of these various soil-forming factors, a diversity of clay minerals is to be expected.

Chemical analysis of the colloids of these soil groups confirms the expected differences in clay minerals. Molecular SiO_2–R_2O_3 and SiO_2–Al_2O_3 ratios of the colloids vary from soil group to soil group and even among individual profiles within the same soil group.

The clay fractions of the various profiles also reflect the influence of the parent materials, but the degree of influence is modified somewhat by eluviation from the A and accumulation in the B horizons, for which the climatic factor is responsible.

From this survey of the South African soils, which contain soil kaolin, montmorillonite, and hydrous mica clay minerals in varying proportions, the following three conclusions become apparent: (*a*) Large regions of South Africa have soils containing soil kaolin, montmorillonite, and hydrous mica clay minerals, and the relationships among them depend on the rainfall, maturity of profile, and parent material. (*b*) The sedimentary parent materials, from which most of these soils are derived, contain clay minerals, and to form a clear picture of the weathering sequence it is essential to determine what clay minerals are present in the soils and in the parent rocks. Unfortunately, for most of the profiles samples of the parent rocks have not been available. (*c*) From the first products of weathering and from the clay minerals in the few samples of parent rocks available, it is evident that during the process of weathering rainfall plays an important part.

In most C horizons of the High Veld prairie soils and in the undecomposed rock (Mt. Edgecombe profile, sample B 1961), the illite-montmorillonoid mixed-layer minerals predominate and soil kaolin is present in small quantities. In the second stage of weathering these mixed-layer minerals are converted mainly to illite and the small amounts of soil kaolin are carried into the B horizons. The conversion takes place in different horizons of the various profiles of the three subgroups, depending apparently on precipitation and temperature. As weathering proceeds under a fairly high rainfall, the soil kaolin becomes the dominant clay mineral in the A horizons of a number of profiles, and illite is in second place. Under a precipitation of 40 or more inches (Darnall and Mt. Edgecombe), soil kaolin is the only clay mineral in the A horizons.

On the A horizons of some profiles (Winburg, Thaba 'Nchu, Cala, Cathcart, and Butterworth) that have developed under a precipitation of 20 to 27 inches a year, illite predominates. The illite-montmorillonoid mixed-layer mineral persists throughout the Cala profile.

Clay minerals of the soils developed from sedimentary rocks under a winter rainfall show very little variation throughout the profile and are inherited from the parent rocks.

In the brown forest soil group, again the clay minerals have been influenced considerably by rainfall. The Messina profile, developed under a low precipitation, has not been affected to a marked degree. As the rainfall increases, montmorillonite disappears entirely, while soil kaolin and, to a lesser degree, illite, appear in the A horizons.

SUMMARY

Clay minerals of the South African podzolic soils and brown forest soil group have been determined by x-ray diffraction and differential thermal analysis. Chemical analysis of the clay fractions was previously reported.

All the podzolic soils developed from sedimentary rocks under a rainfall high enough to produce leaching and differentiation into the various horizons. The

soils were divided into subgroups according to their morphological characteristics. Brown forest soils are derived from acid and basic igneous rocks under a rainfall ranging from 12 to 26 inches a year.

Chemical composition of the colloids and derived data indicate that normally a variety of clay minerals can be expected in these soils. By x-ray diffraction and differential thermal analysis colloids of the soils in these soil groups were found to consist of soil kaolin, montmorillonite, and illite-montmorillonoid mixed-layer minerals. The clay minerals of parent rocks and the first products of weathering of some podzolic soils are generally illite-montmorillonoid mixed-layer and montmorillonite or both. As weathering proceeds, illite and soil kaolin predominate, and if rainfall is high enough, the latter is the only clay mineral present. Some soils retain unaltered to maturity the clay minerals inherited from the parent rock.

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Air Pollution and Community Health. By CLARENCE A. MILLS. The Christopher Publishing House, Boston, 1954. Pp. 180. Price $2.75.

The author, who is professor of experimental medicine, University of Cincinnati, presents a disturbing picture of the effects of industrial gases and dusts, plus those emanating from household flues, on the health of persons living in surrounding areas, particularly lower-lying areas. He reviews the Donora smog disaster and then explores conditions as they were and continue to be around some of our larger cities, notably Pittsburgh, Detroit, Atlanta, Los Angeles, and Mexico City. Considerable improvement has been effected in all these areas, but only after organized effort to force the issue. Much of the material presented is repetitive, but the reader has no difficulty understanding the nature of the problems and what is involved in their solution.

Bibliography of Plant Protection. By JOHANNES BARNER. Biologische Gundesantalt für Land- und Forstwirtschart, Verlag Paul Parey, Berlin, 1955. Pp. 420. Paper-bound.

This volume, in German, English, and French, includes some 12,500 titles for 1951. The earlier 22 volumes, begun by Dr. Morstaat in 1921, covered the years 1914–1945. Subsequent volumes are expected to close the gap between 1945–1951. The first part of this volume deals with books and congresses; the second, diseases and causes; the third, diseases and host plants; and the fourth, measures for plant protection. The bibliography covers the work of some 8,500 authors. Although of particular interest to plant pathologists, it also reports on diseases of nonparasitic origin, including deficiency diseases, climatic influences, industrial and pest-control damage, and wounds.

Directory of Wheel and Track-Type Tractors. By the FOOD AND AGRICULTURAL ORGANIZATION OF THE UNITED NATIONS. Columbia University Press, New York, 1956. Pp. 371. Price $3.

This report, which covers the entire world, is presented in English, French, and Spanish. It gives addresses of manufacturers and lists wheel and crawler tractors by categories and specifications of models.

Inland-Dune Sand Soils. By J. SCHELLING. Soil Survey Institute, Wageningen, The Netherlands, 1955. Pp. 57. Paper-bound.

This publication, written in Dutch, contains a three-page summary in English. The purpose of the reported study was to find the explanation of differences in forest growth that occur from point to point. These differences were found to be due to differences in organic matter content of blown sand caps, to presence or absence of buried soil profiles, to the depth of the cap, and to the rooting habits of trees. Dry inland-dune soils are given a provisional classification, and a series of six color maps is appended.

Inorganic Nitrogen Metabolism. Edited by WILLIAM D. MCELROY AND BENTLEY GLASS. Johns Hopkins Press, Baltimore, 1956. Pp. 728. Price $10.

This book contains addresses and discussions from a symposium held at the McCollum-Pratt Institute June 21–23, 1955, which was concerned as a central problem with the intermediate steps and mechanisms involved in the production of proteins in plants from free nitrogen or nitrate. The role of molybdenum received special emphasis. The papers were written by some 60 scientists, including A. J. Anderson and A. T. Dick of the Commonwealth Scientific and Industrial Research Organization of Australia, where the need for molybdenum in plant nutrition was first demonstrated in field agriculture and where the known need for the element is much greater than in any other region. Other than those presenting papers, 75 persons participated in the discussion. The last chapter is an excellent summary of the symposium. This book is extremely interesting and highly important for soil-plant scientists concerned with these problems.

Mulching. By G. V. JACKS, W. D. BRIND, AND ROBERT SMITH. Commonwealth Agricultural Bureau, Farnham Royal, Bucks, England, 1955. Pp. 87, figs. 17. Price 15/.

This is Technical Communication 49 of the Commonwealth Bureau of Soil Science. The introduction defines mulches, with particular reference to the dust and stubble forms, and gives results in terms of crop yields. Part I presents data on the effects of mulching on moisture, temperature, and the microbial, chemical, and physical properties of soils. The remainder of the book describes stubble-mulch equipment, farming systems in which it is employed, and experimental results with these systems in the United States, notably in the subhumid regions. All the illustrations are from photographs taken in the United States and Canada. A list of some 275 references is appended. Particular attention is given to the work at the Agricultural Experiment Stations in Nebraska, Iowa, Ohio, Michigan, Virginia, New York, and Indiana. A first-class review of the subject.

Nellie Landblom's Copybook for Beginners in Research Work. By NELLIE THOMPSON LANDBLOM. Colorado Agricultural and Mechanical College. Multigraph Service Bureau, Fort Collins, 1955. Pp. 118. Price $2.95. Multigraphed, paper cover.

The author, a mathematician by training and experience, assumes that the reader has preliminary knowledge of the fundamental principles of statistics, and, as a result, knows which model to use and how to interpret results. The book is divided into two parts. The first consists of 26 chapters dealing with the randomized block, the Latin square, the factorial, split plot, and other designs, and it considers the problems involved in dealing with the data assembled from their use. The second part concerns an experiment on "adjusting beef cattle weaning weights for certain environmental variables by the fitting of constants." The data came from a study of 546 Hereford calves under the direction of H. H.

Stonaker of the animal husbandry department of Colorado A. and M. The important feature of this manual is the detail in which problems presented are solved.

Present Status of Investigations on the Use of Wood Residues for Soil Improvement in the United States. By H. W. Reuszer, R. L. Cook, and E. R. Graham. Purdue University, Lafayette, Indiana, 1955. Pp. 13. Multigraphed.

This report of a work group of the North Central Soil Research Committee can be obtained by writing to H. W. Reuszer at Purdue University. The other two members of the committee are associated with Michigan State University and the University of Missouri, respectively. In respect to wood residues, the report considers toxicity and pH effects; nitrogen relationships; effects on physical, chemical, and microbiological properties of soils; use as bedding and in composts; and optimum amounts to add to the soil. A list of 43 references is appended.

Rocks and Minerals. By Richard M. Pearl. Barnes and Noble, Inc., New York, 1956. Pp. 275, figs. 35, color plates 12. Price $1.95. Paper-bound.

One of the "Everday Handbook Series" that covers a wide variety of topics, including business, culture, guidance, handicrafts, recreation, literature, and science, the current volume, like its predecessors, is designed to give the general reader a quick review of the more salient facts on the subject. It covers definitions, prospecting, mining, identification, classification, origin, crystals, gems, atomic and luminescent minerals, ores, oddities, man-made minerals, and collections. The 12 color plates contain 36 separate units. Unexpected topics, such as "Stones from the Sky," are included. The author points out that some 400 million meteorites enter our atmosphere daily but only a few survive to reach the earth. Yet some twenty thousand to fifty thousand years ago a gigantic meteorite tore a hole 4,250 feet wide and 570 feet deep in Arizona. Suggestions for supplemental reading and a glossary are appended. This is a highly interesting book.

Rural Appraisals. By Earl F. Crouse and Charles H. Everett. Prentice Hall, Inc., Englewood Cliffs, New Jersey, 1956. Pp. 531, figs. 39. Price $6.75.

The authors are associated with the Doane Agricultural Service, Inc., St. Louis, Missouri, and the book is dedicated to Dr. Howard Doane, the originator of the company. The book details the use of the American Rural Appraisal System as applied by the company since 1936. Earning power, location, neighbors, and soils are carefully considered, as are maps and reports. Renting, ownership, specialized crops, heavy fertilizing, building values, and obsolescence are also discussed. Appraisals for court, tax, and loan purposes, too, are included. Two chapters are devoted to the soil phase of the problem. The final chapter deals with the profession of rural appraising. An extended appendix of 31 items contains a great variety of highly useful information. Anyone who owns a farm, wants to own one, rents one, or runs one will find this a very valuable book.

Where There Is Vision. By Ingrid Nelson Waller. Rutgers University Press, New Brunswick, New Jersey, 1955. Pp. 284. Price $5.

This is an attractively written history of the New Jersey Agricultural Experiment Station and was published as a part of the celebration of its 75th anniversary. It deals primarily with the record of research findings of the last 25 years. Some idea of the nature of the presentation can be gleaned from the chapter headings. Among the 30 headings are: "It All Begins with the Soil;" "Rutgers—a Super-Tomato;" "Fifty Kinds of Peaches;" "Blueberry Pie and Cranberry Sauce;" "Pig Pens and Race Tracks;" "Doctors to 20 Million Birds;" "Salt Water Farming;" "Battle of the Bugs;" "Police at Work;" "Voice of Educators"; and "Making the Wheels Go Round." The subtitle of the book is "Seekers of Truth and Dreamers of Great Dreams." Every experiment station worker will find this of great general interest and of special value in relation to his own field of endeavor.

The Editors

NOTES

A Portable Power-Driven Soil Sampler[1]

Recently the Haynes Manufacturing Company of Livingston, Texas, in cooperation with the authors, developed and tested a mechanized soil sampler that weighs only 35 pounds and can be carried by one person (fig. 1).

The "Little Beaver" soil-sampler power unit consists of a back pack-mounted 2-cycle gasoline engine developing 2.5 horsepower. Energy is transmitted to a step-down transmission via a centrifugal clutch and a flexible drive cable. The throttle is conveniently located on the handle of the transmission head. The soil auger is attached to the transmission by means of an adapter and a snap-on connection that makes coupling and uncoupling very easy.

Three types of augers have been developed for the power unit (fig. 2). The total length of an auger plus shaft is 42 inches; 36-inch snap-on extensions are available for deep sampling. Six-inch intervals are marked on shafts and extensions. To permit easy withdrawal from the sample hole, each auger has a slight taper toward the upper end.

The cost of the outfit ranges from $275 to $325, depending on the sampling attachments desired.

Time tests were made on two rather diverse soils of east Texas: a Boswell fine sandy loam (3 to 5 inches of fine sandy loam A horizon underlain by a heavy, plastic B horizon), and a deep-phase Lakeland fine sand (loose fine sand more than 6 feet deep). For each soil, three test holes were sunk to a depth of 6 feet, which involved drilling 6 to 12 inches at a time, pulling the auger out of the hole, removing the sample from the auger, and cleaning the auger bit before each new drilling. One extension was used in the lower depths.

The total elapsed time, in minutes, for each of the three sample holes for the two soils was:

Hole No.	*Boswell*	*Lakeland*
1	9.50	10.00
2	9.25	5.25
3	8.00	6.75

The spiral auger was used in the Boswell soil, the bucket type in the sandy Lakeland. Noteworthy in each case was the ease with which the augers were removed from the holes. Even in the heavy clay subsoil of the Boswell the auger was much easier to extract than the conventional hand auger.

The equipment was also tested with a variety of other east Texas soils, including some with considerable amounts of gravel, and, except on stony soils, gave very

[1] From the U.S. Department of Agriculture (E. R. Ferguson, Southern Forest Experiment Station, Forest Service, and R. M. Voigtel, Soil Conservation Service) and the Stephen F. Austin State College, Nacogdoches, Texas (J. L. Smith). Received for publication November 21, 1955.

Fig. 1 The Power Soil Sampler in Operation
The 2½ horsepower motor is ample for the toughest clays

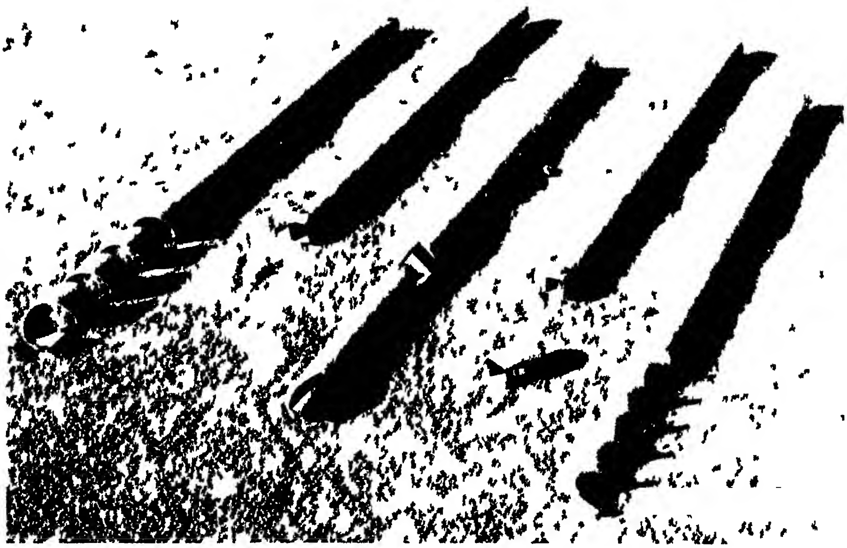

Fig. 2 Three Available Interchangeable Augers
All three augers are 2½ inches in diameter and 12 inches long. The spiral auger (*left*) is designed to operate in all medium and fine textured soils between field capacity and wilting point, the bucket auger (*center*) in dry sands, and the screw auger (*right*) in extremely plastic clays, shales or gumbos.

satisfactory results. It was the opinion of men experienced in soil sampling that the machine is much faster and much easier to operate than the hand auger and that it permits sampling under conditions that preclude use of the conventional auger. Samples taken by this tool do not preserve soil structure; where undisturbed samples are required the machine can be used to sink a hole nearly to the desired depth and the core can then be taken with a hand sampler of the San Dimas type.

E. R. Ferguson, R. M. Voigtel, and J. L. Smith

How to Eliminate Clogging in Direct Determination of Soil Exchangeable Cations by the Beckman Flame Spectrophotometer[1]

In the direct determination of bases in soil extract with ammonium acetate solution, the gradual clogging of the burner, appreciably affects the readings and constitutes a serious drawback to that method. Carbon deposited at the opening of the burner was seemingly the main source of trouble. A solution suggested by Dmitrieff-Kokline[2] as wettable, viscid, and alkaline enough to keep the burner from deteriorating, and composed of redistilled water containing 10 per cent ethyl alcohol and 0.5 per cent triethanolamine, was studied with a view to stopping such clogging. Thus, the ammonium acetate solution containing the exchangeable cations was evaporated to dryness, and an attempt was made to dissolve the residue with Dmitrieff-Kokline's alcoholic solution. Unfortunately, solubilization of calcium and magnesium acetate in that solution was found to be very low.

The following technique was therefore devised. An aliquot of extracted ammonium acetate solution is diluted half and half with Dmitrieff-Kokline's alcoholic solution and finally subjected to analysis by means of the Beckman flame spectrophotometer, model DU, with photomultiplier attachment. The standard solutions used contain all four cations to be analyzed, and the solvent is made of equal parts of the alcoholic and ammonium acetate solutions.

The method has been found very satisfactory. In more than 6000 determinations made with the same burner, neither clogging nor carbon deposits have been observed. Since the dilution of the ammonium acetate extract would make determination of Mg difficult on many soils containing small amounts of this cation, the background is lowered by flame adjustment at 8 pounds per square inch for both oxygen and acetylene.

Lucien Choinière

[1] From the Quebec (Canada) Department of Agriculture, Provincial Soils Laboratory, Ste-Anne de la Pocatière. Paper translated from the French by Dr. G. J. Ouelette, Ste-Anne de la Pocatière. Received for publication December 19, 1955.

[2] Dmitrieff-Kokline, A. Amélioration de la reproductibilité du spectrophotomètre à flamme de Beckman (modèle DU). *Ann. ACFAS* 18: 86. 1952.

To Hold Fifth National Clay Conference

The Fifth National Clay Conference will be held at the University of Illinois, Urbana, October 8, 9, and 10. The conference is sponsored annually by the Clay Minerals Committee of the National Academy of Sciences—National Research Council, under the chairmanship of Prof. R. E. Grim of the University of Illinois.

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CLAY MINERALS IN SOME LIMESTONE SOILS FROM ISRAEL

I. BARSHAD, E. HALEVY, H. A. GOLD, AND J. HAGIN

University of California, Berkeley[1]

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Soils formed from limestone and dolomitic parent materials have been divided into two main groups: the rendzinas—white, gray, or gray-brown soils; and the terra rossas—predominantly red soils. Many investigators (13, 20) have suggested that the hardness of the parent rock determines the product. Thus, rendzina is associated with relatively soft limestones, whereas terra rossa is a product of hard limestones and dolomites. Several theories explaining the formation of terra rossa have been postulated, but the one proposed by Reifenberg (18) is the most widely accepted.

Although many data relating to soils derived from calcareous parent materials are available, very few deal with the nature of the clay minerals, chiefly because the analyses were carried out prior to recognition of the true nature of clay minerals in soils. This situation, however, is being rectified. The presence of illite, montmorin and kaolin type minerals, and attapulgite in limestones and calcareous soils was reported by some investigators (5, 7, 8, 11, 15, 16, 17, 19, 21). Previously reported attapulgites (9, 12) were also associated with limestone.

Determination of the clay minerals in the profiles of rendzinas and terra rossas will reveal whether the two soil groups are actually different. The present study, therefore, was undertaken to determine, by the most advanced methods, the nature of the clay minerals in a group of soils from an extensive limestone area—Israel. Nearly all the soils in Israel have been derived from limestones.

MATERIALS AND METHODS

Description of soils

Sampling places were chosen to provide soils developed on various limestones and also to represent some of the soil groups that cover large areas in the country. The soils do not represent any soil series. For this investigation they were designated by numbers (table 1).

Eilon. A dark reddish brown soil, representative of the terra rossa soils which comprise large areas in the Galilea hills. The rocks are from the Upper Cenomenian formation.[2]

[1] J. Hagin is at the College of Agriculture, Hebrew University, Jerusalem.

[2] Geological data were obtained from the geological map of Palestine by Black and from personal communication with Mr. M. Ben-Yair.

TABLE 1

Designation of soils according to location and depth

Location	Hulda	Eilon	Taoz	Gilat	Eshtaol	Hanita
Profile Designation	1	2	3	4	5	6
Layer designation	Depth of Layer					
	cm.	*cm.*	*cm.*	*cm.*	*cm.*	*cm.*
a	0–10	0–5	0–20	0–18	0–16	0–12
b	10–47	5–23	20–70	18–39	16–44	12–38
c	47–82	23–40	70–130	39–84		38–68
d			130–160	84–120		
e	82–	40–	160–	—	44–	68–

Hanita. Also a sample from Galilea. A light yellowish brown soil generally found on soft limestone and in patches between the red soils. The bedrock is a Senonian formation.

The next three samples are representative of the hilly section in central Israel which ascends from the coastal plain to Jerusalem. In the higher parts, near Jerusalem, red or red-brown soils similar to the Eilon profile are found. The sequence of the samples is from west to east.

Hulda. A dark gray-brown soil from a forested site in the foothills. The bedrock is a Lower Eocene formation.

Taoz. A very pale brown soil, fairly representative of the central hilly section. The bedrock is an Eocene formation.

Eshtaol. A grayish-brown soil sampled in the higher hilly section bordering the red soils of the Judean mountains. The bedrock is a weathered lithographic limestone from a Turonic formation.

Gilat. A light yellowish brown soil representative of the loess soils from the arid region of Israel, the Negev. It is a deep secondary soil.

In Israel winters are rainy and summers dry and warm. The yearly amount of rainfall in Galilea is about 600–800 mm. and in the Hulda-Eshtaol region about 400–600 mm.

Experimental methods

Mechanical analysis of the whole soil. The American Society for Testing Materials method (1) was used with hydrometer type 152H. Stirring time was modified to 5 minutes.

Extraction of clays. Clay fractions of $< 2\mu$ and $< 1\mu$ were separated. To preserve the natural mineralogical composition of the clay fractions, a dispersing agent was avoided. The extracted clays were treated with 30 per cent H_2O_2 until nearly all the organic matter was destroyed. The clays were then air-dried, ground to pass a 60-mesh sieve, and stored in air-tight bottles for use in various analyses.

Differential thermal analysis. Differential thermal analysis, as modified by Barshad (2) was used: rate of heating was 9° a minute, and platinum–platinum-10 per cent rhodium thermocouples in a nickel block were used. Volume of samples was kept constant (0.2355 ml.), and weights were recorded. The weight of

samples ranged between 0.2500 and 0.3500. Both natural and acid-treated clay samples were analyzed. The acid treatment involved removal of carbonates with cold 0.3 *N* HCl and subsequent removal of the salts and acid with distilled water.

Integral thermal analysis (dehydration curve). The integral thermal analysis method was used to determine adsorbed water, crystal lattice water, and CO_2 from the carbonates. The data obtained by this method were used as an independent check on results of the differential thermal analysis and of the carbonate determination by chemical analysis.

X-ray analysis. X-ray analysis was performed with Cu $K\alpha_1$ radiation. Filtration of the x-rays was accomplished by taping a nickel foil on the inlet end of the pinhole collimator. Samples were prepared by: (*a*) Barshad's sodium-citrate–sodium-hydrosulfate method (3); (*b*) untreated air-dried sample in a glass capillary; and (*c*) untreated and HCl-treated air-dried or glycerol-wet samples placed in the center of a copper ring sample-holder between two sheets of mylar.[3]

Electron microscope analysis. The RCA-EMU2B microscope was used to examine the clay fractions. The shadow technique method was employed in preparing the materials, and several electron micrographs were taken of each mount.[4]

Cation-exchange capacity determination. The ammonium acetate method was used to measure the exchange capacity of the clay fractions in the natural state and of the HCl residue of the parent materials.

Carbonate analysis. Williams' method (23) was used to determine the carbonate content of the materials. The Ca^{++} and Mg^{++} associated with the carbonates were determined by extracting the samples with a cold solution of 0.1 *N* HCl and KCl and determining, in the solution, the Ca^{++} and Mg^{++} by ethylenediaminetetraacetic acid (14) as well as by standard gravimetric procedures. The residue from the foregoing treatment was determined after washing it free of the acid and salt solution with water and drying it at 110°C.

Potassium determination. Groves' (10) method was used to determine the total K_2O content of the clay fractions as a means of verifying the presence of the mica clay minerals.

Analysis of the HCl extract of the parent material. Groves' (10) outline for total analysis of silicates, with slight modifications, was followed in the analysis of the HCl extract of the parent material. Silica and sesquioxides were determined gravimetrically. Ca^{++} and Mg^{++} were determined volumetrically.

Determination of the residue content. In determining the amount of residue, the material left after HCl-extraction of the carbonates, 1.00, 16.00, and 50–200 g. of ground rock were used. The residue of the parent material was subjected to the same analyses as the clay fractions of the soils.

RESULTS

The results obtained by the various analyses are divided into two parts: those dealing with the qualitative identification of the constituents of the materials

[3] Unpublished method of I. Barshad.

[4] Analyses made by Herbert A. Gold of the plant pathology department.

examined, and those dealing with the quantitative estimation of these constituents.

Identification of constituents

The result of the x-ray analysis (tables 2 and 3) and those of the electron microscope (fig. 1) clearly identify all of the constituents present. These are clay minerals belonging to the montmorin and the kaolin groups and one unusual clay mineral for soils—attapulgite. This is the first report of the presence of attapulgite in relatively large amounts in soils over as large an area as the whole of Israel. Because of the interference of attapulgite, presence of a mica-clay

TABLE 2

*Interplanar spacings and estimated intensities in x-ray powder diagrams of glycerol-wet <2μ clays**

Spacing	Mineral	Intensity†					
		1a	2a	3a	4a	5a	6a
A.							
17.7‡	Montmorin	s	m	m-s	m-s	s	s
10.4	Attapulgite	w		s	m-s	vw	w
7.2	Kaolin	m-w	m-s	vw	m	w	vw
6.4	Attapulgite	vw		vw	vw	vvw	vw
5.4	Attapulgite	w		wm	w	vw	vw
4.5	Montmorin-kaolin	s	s	m	s	m	m-w
3.35	Quartz	m-w	m-s	w	m	m	m
3.03§	Calcite	ms		vs	vs	vs	vvs

* Values for Cu Kα, radiation (1.5374 A.).

† vvs = very very strong; vs = very strong; s = strong; m = medium; w = weak; vw = very weak; vvw = very very weak.

‡ Spacing becomes 15 A. when sample is air-dried and 10 A. when heated to 250°C.

§ Line disappears upon acid treatment and sodium-citrate treatment.

TABLE 3

*Interplanar spacings and estimated intensities in x-ray powder diagrams of glycerol-wet, HCl-insoluble residue of the parent materials**

Spacing	Mineral	Intensity†				
		1e	2e	3e	5e	6e
A.						
17.7‡	Montmorin	m-s	m	w	s	s
10.4	Attapulgite	s		vs	w	m
7.2	Kaolin	w	m-s	vw	w	w
6.4	Attapulgite	vw		w	vw	vw
5.4	Attapulgite	w		m-w	vw	vw
4.5	Montmorin-Kaolin	m	s	m	m-s	m
3.35	Quartz	m	m-s	m	w-m	m

* See note table 2.

† See note table 2.

‡ See note table 2.

mineral could not be definitely ascertained by means of x-ray analysis, but chemical analysis for total K_2O disclosed small amounts of a mica-clay mineral. Among the nonclay minerals, calcite was found to be the most abundant in all samples except the terra rossa (profile 2), and quartz was also present in nearly all the soils.

The montmorin clay minerals were most readily identified by x-ray analysis from the variable d(001) spacing, which assumed a magnitude of 17.7 A., 16.5 A., 15 A., and 10 A., according to the pretreatment.

The kaolin minerals were also readily identified by x-ray analysis from the 7.2 A. d(001) spacing and also by the electron micrographs in which the kaolin particles appear hexagonal and opaque.

The attapulgite clay mineral was first identified in the x-ray diagram by the presence of a relatively intense, sharp, and constant spacing at 10.4 A. The presence of very little K_2O in the clay samples indicated that the 10.4 A. spacing could not belong to a mica clay which also registers a spacing very close to 10 A. The presence, therefore, of the 6.4 and 5.4 along with the 10.4 A. spacings led to the conclusion that the clay mineral must be attapulgite, since these three spacings are some of the most characteristic spacings of this mineral (6). This conclusion was completely verified by the electron-microscope analysis, by which the attapulgite particles appear as needle and rod-shaped particles and as bundles of needles (fig. 1).

Calcite was readily identified in the x-ray diagrams by the intense and sharp spacing at 3.03 A., which disappeared on treatment with 0.1 N HCl or sodium citrate. No other carbonate minerals were identified in the x-ray diagrams.

Quartz was identified in the x-ray diagrams by the 3.35 A. spacing and also in the electron micrographs as irregularly shaped and angular particles.

Differential thermal analysis of clay minerals. Montmorin and kaolin are also readily identified by the differential thermal analysis curves (fig. 2A). The exothermic breaks in the curves, in the temperature range between 800° and 1000°C., which are usually associated with montmorin and kaolin, are in the present samples strongly affected by the presence of calcite. This effect is due to the occurrence of the endothermic break, associated with the decomposition of the carbonates which either cancel out the exothermic break of the clay minerals completely (fig. 2C) or bring about a split in a single exothermic break, resulting in the appearance of two breaks (fig. 2D). These curves, therefore, are excellent examples illustrating the difficulties in identification of constituents in samples with a varied mineralogical composition.

Identification of attapulgite by means of differential thermal analysis is impossible in presence of montmorin and kaolin. The breaks of attapulgite may overlap the break of montmorin at the low temperature range and that of kaolin at the intermediate temperature range (fig. 2E). In the present study, differential thermal analyses were of no aid in the identification of attapulgite.

Differential thermal analysis curves of clay carbonates. The endothermic breaks associated with decomposition of carbonates in the differential thermal analysis curves are of particular interest analytically because they represent

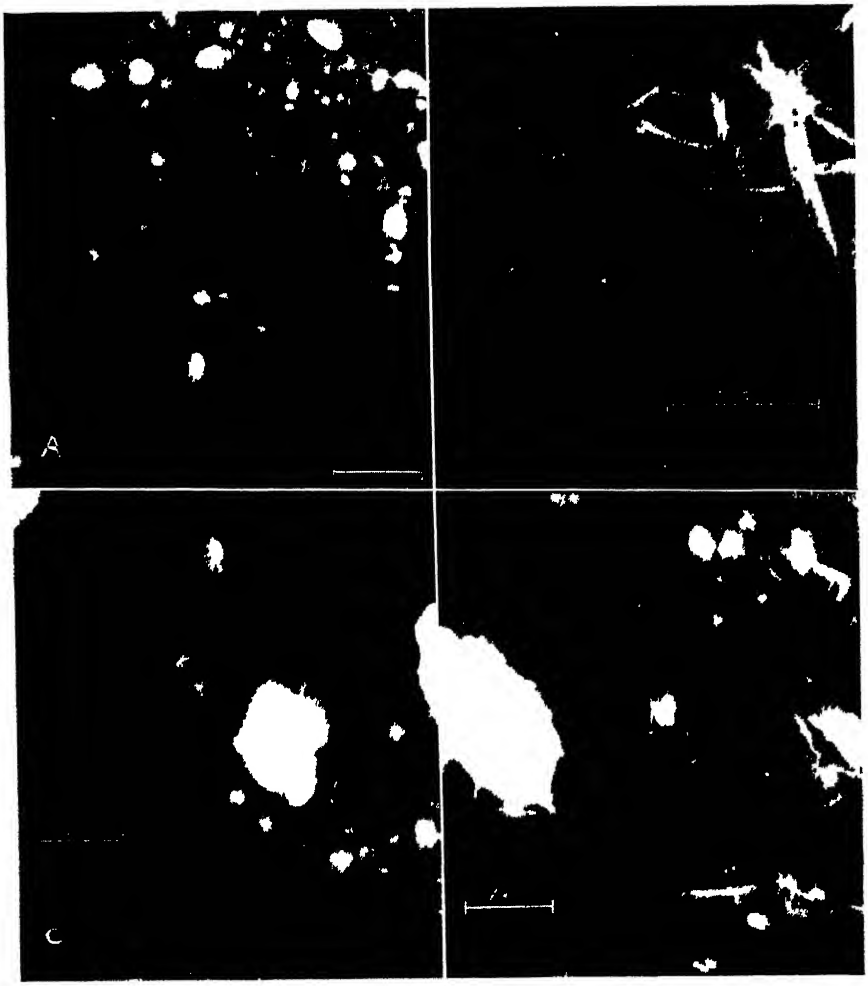

FIG. 1. Electron Micrographs of Representative Clay Fractions. A 2a, $<2\mu$; B. 3e; C 4a, $<2\mu$; D 5a, $<2\mu$

certain departures from the standard differential thermal analysis breaks of the pure carbonate minerals (22). These departures are as follows: The initial temperature at which the breaks start is lower by about 100° to 200°C. (fig. 2B and F); the break extends over a broader range of temperatures, from 600° to 950°C. rather than from 800° to 900°C. (fig. 2F); and instead of a single peak the break may contain two or three peaks (fig. 2F). The cause for these deviations may possibly be attributed to three factors: (*a*) the smaller particle size of the carbonates in the clay samples as compared with those in ground minerals, as shown with dolomites by Bradley *et al.* (4); (*b*) the presence of $MgCO_3$ as impurities in the calcite, as shown by the chemical analysis (table 4); and (*c*) the occurrence of exothermic reactions associated with other minerals than the

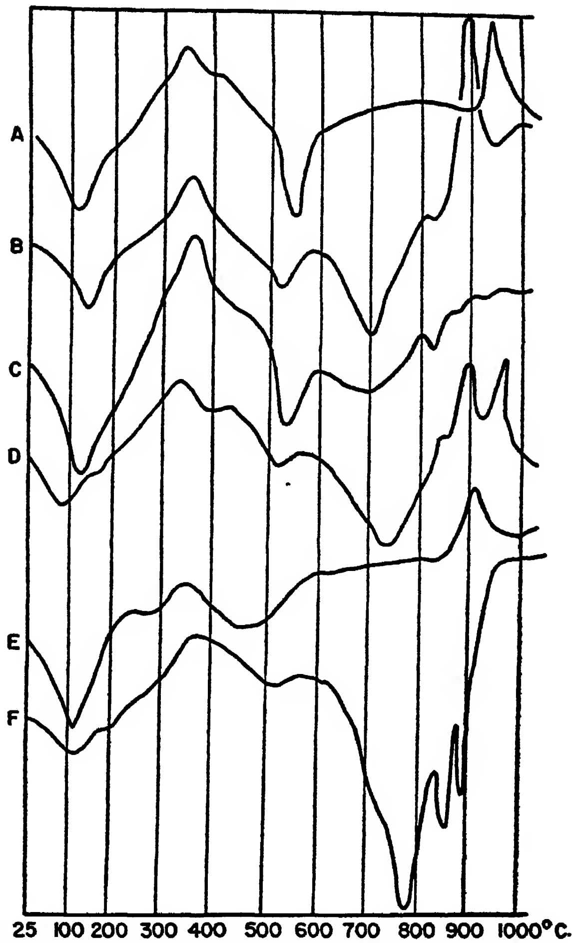

FIG. 2. Differential Thermal Curves of Some Clay Fractions. A. 2a, <2μ; B. 3d, <1μ; C. 1a, <1μ; D. 5a, <2μ; E. Attapulgite (Union Oil Co.); F. 6c, <1μ

carbonates in the sample. These exothermic breaks may offset partly or completely the endothermic break of the carbonates if the quantity of carbonates is small, or they may cause the appearance of more than one peak in the carbonate endothermic break. Although the x-ray diagrams of these samples and the chemical analysis indicate the presence of large amounts of carbonates, the differential thermal analysis curves indicate the presence of relatively smaller amounts.

Chemical analyses. Chemical analyses were confined to: (*a*) use of acid for liberation of CO_2 from carbonates and for its effect on the x-ray diagrams (table 3) and on the differential thermal analysis curves (fig. 2); and (*b*) the cation-exchange capacity determination. Table 5 shows that the capacities are relatively high, indicating the presence of large proportions of montmorin minerals.

TABLE 4

Chemical composition of <2μ clay fraction and parent material

Sample	$CaCO_3$	$MgCO_3$	Total Carbonates	H_2O^-	R_2O_3*	SiO_2*	Acid-Insoluble Residue	Total Constituents	Total K_2O in Residue	$\frac{CaCO_3}{MgCO_3}$	$\frac{R_2O_3}{Residue}$
	%	%	%	%	%	%	%	%	%		
1a	11.53	0.80	12.33	10.81	1.43		76.00	100.57	0.63	12.1	0.019
2a	0.00	0.00	0.00	7.10	1.00		92.73	101.83	0.24		0.011
3a	43.20	2.47	45.67	7.96	1.50		46.15	100.28	0.59	14.7	0.032
4a	24.36	2.58	26.94	6.48	6.53		60.45	100.45	1.20	7.9	0.108
5a	42.27	0.98	43.25	6.04	3.25		47.60	100.14	0.60	36.5	0.063
6a	72.28	0.59	72.87	2.49	2.51		22.00	99.83	0.31	104.0	0.114
1e	95.95	1.59	97.54		0.49	0.13	2.53	100.69		50.8	0.194
2e	81.31	18.62	99.93		0.28	0.06	0.19	100.46		3.68	1.475
3e	87.48	3.71	91.19	4.7†	0.99	0.45	1.67	99.00		19.9	0.593
5e	95.00	2.53	97.53	1.0†	0.39	0.07	1.16	100.15		31.6	0.337
6e	88.94	0.53	89.47		1.00	0.49	9.53	100.49		128.6	0.105

* In HCl extract.

† H_2O + organic matter.

Integral thermal analysis. Use of integral thermal analysis as a means of identification of clay minerals is not very satisfactory for materials with a composition as varied as those in the present study. But the weight loss at temperatures up to 200°C., representing water loss, and the weight loss above about 300°C., representing, in the sample studied, loss of CO_2 and crystal lattice water, are aids in estimating relative montmorin content and amount of carbonates. Losses above 300°C. would represent kaolin minerals if the main loss occurred at about 400–450°C. or carbonates if the main loss occurred at temperatures above 450°C. For the samples studied (table 5 and fig. 3) the weight losses at 200°C., when expressed on a $CaCO_3$-free and oven-dry basis are relatively high, ranging from 12.4 to 17.3 per cent, indicating, therefore, the presence of large amounts of montmorin, whereas the losses above 300°C. represent mainly losses in CO_2.

Quantitative estimation of carbonates and clay minerals

Carbonates. Of all the constituents of the clay fractions and of the parent materials, the carbonates were the most accurately determined by means of chemical analysis. The values (table 4) were calculated on the assumption that Mg^{++} found in the HCl-extract is present wholly as carbonate, whereas the Ca^{++} represents both exchangeable Ca^{++} and Ca^{++} in the carbonate fraction.

In the clay fraction the sum of Ca^{++} and Mg^{++} exceeded the CO_3^{--}, whereas in the parent materials the CO_3^{--} exceeded the sum of Ca^{++} and Mg^{++}. The excess of bases over the CO_3^{--} in the clay fraction is due to the fact that the bases in the HCl extract include, in addition to the carbonate bases, the exchangeable bases, which, for the sample studied, are equal to the cation-exchange capacity, together with a certain amount of nonexchangeable bases released as a result of a slight decomposition of the clay minerals by the acid treatment. On the other hand, the excess of CO_3^{--} over the bases in the parent materials may be

TABLE 5

Cation-exchange capacity, water losses, and CO_2 content in <2μ clay fractions

	1a	2a	3a	4a	5a	6a
C.E.C.* me./100 g. air-dry	70.3	49.1	31.7	42.9	36.1	22.5
C.E.C. me./100 g. air-dry carbonate-free	78.2	49.1	54.2	58.8	65.9	90.8
C.E.C. of parent material HCl-residue†	60.0	42.0	38.0		65.2	71.6
C.E.C. me./100 g. oven-dry carbonate-free	87.5	52.5	62.0	64.1	73.6	100.5
H_2O^- per cent, carbonate-free basis‡	12.2	7.0	14.4	9.1	11.6	10.9
Loss at 200° C., per cent carbonate-free, oven-dry at 200° C.	15.4	9.7	17.3	12.4	15.9	16.8
Loss in weight 300–800° C., per cent†	9.37	6.54	16.7	16.6	21.6	38.5
CO_2, per cent†	4.4	0	16.6	10.8	18.0	30.0
Δ loss in weight (300–800° C.) − (CO_2) per cent†	5.0	6.5	0.1	5.8	3.6	8.5

* C.E.C. = cation-exchange capacity.
† On air-dry weight of sample.
‡ Loss at 110° C.

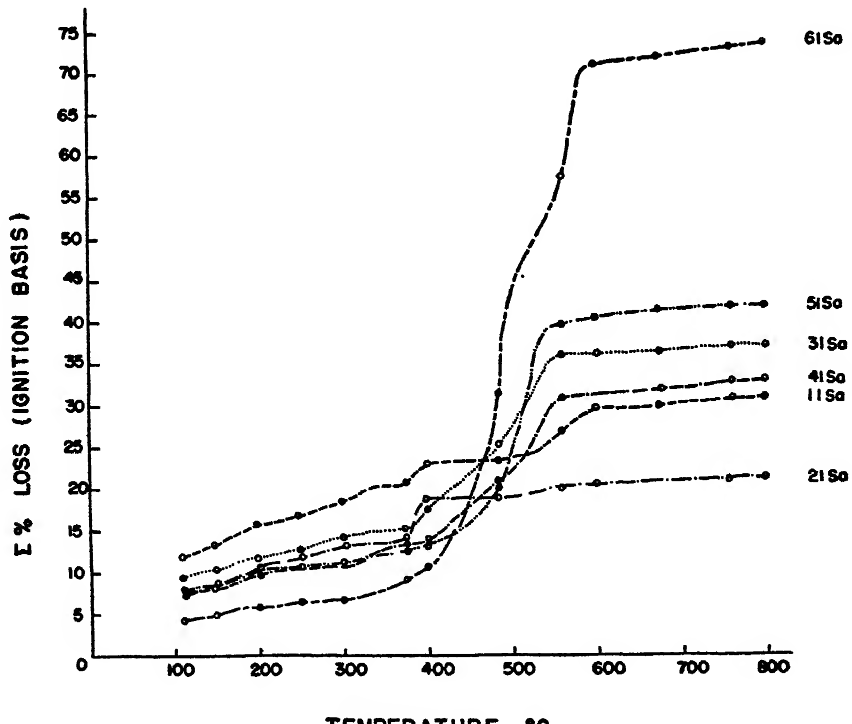

FIG. 3. Integral Thermal Analysis Curves of <2μ Clay Fractions.

due to the fact that some of the CO_3^{--} represents carbonates combined with cations not determined in the present study. In all the materials studied, Ca^{++} greatly exceeds Mg^{++}; in fact, the x-ray diffraction diagrams indicate the presence of only calcite. The Mg^{++}, therefore, must be present as an impurity within the

calcite. Total carbonates in the clay fraction range from 0.0 in soil 2 (the terra rossa) to 72.87 per cent in soil 6; in the parent materials the carbonate content ranges from 89.5 to 99.9 per cent. When both the CO_3^{--} content, expressed as CO_2, and the loss in weight between 300–800°C. are expressed as percentages of the air-dry natural material and compared (table 5), the latter is seen to be mainly due to the evolution of CO_2. The weight losses in excess of the CO_2 represent crystal lattice water.

The ratio $CaCO_3/MgCO_3$ (table 4) in the clay fractions ranges between 7.9 and 104, whereas in the parent materials the range is from 3.68 to 128.6. On the basis of these ratios, only the parent material of the terra rossa soil may be said to represent a dolomite.

Clay minerals. The mineralogical composition of the insoluble residue of the clay fractions and the parent materials are shown in table 6. The montmorin, kaolin, and attapulgite content are expressed on a percentage basis—the sum being 100 per cent. Although this sum does not constitute the whole of the residue, it is equal to the whole of the clay mineral content. The clay minerals, however, constitute 80 to 95 per cent of the residue, the remainder consisting of quartz, mica, and amorphous sesquioxides. No attempt was made, in the present study, to determine these quantitatively.

The clay minerals were estimated quantitatively as follows: kaolin, from differential thermal analysis curves by the area of the endothermic break in the temperature range between 455 and 575°C.; attapulgite, from the relative abundance in the electron micrographs and from the relative intensity of the 10.4 A. spacing in the x-ray diagrams; and montmorin, by difference and also from the relative intensity of the 15 A. spacing in the x-ray diagrams, the exchange capacities, and the water content at 200°C. Generally, it may be assumed that the higher the

TABLE 6

Mineralogical composition of HCl-insoluble silicate residue of <2μ clay fraction of soils and parent materials

Sample	Montmorin	Kaolin	Attapulgite	Mica*	Quartz*
	%	%	%		
1a	78	14	8	x	x
1e	48	2	50	x	x
2a	65	35	0	x	xx
3a	17	3	80	x	x
3e	7	3	90	x	x
4a	55	10	35	xx	xx
5a	50	25	25	x	x
5e	40	20	40	x	x
6a	78	2	20	x	x
6e	60	1	39	x	x

* x indicates mere presence; xx, presence in more substantial quantities.

exchange capacity, the larger the montmorin content. Similarly, the higher the adsorbed water content, the higher the montmorin content. Since attapulgite, however, also has a large capacity for water adsorption, this latter relationship is completely disturbed in the present samples, as is clearly demonstrated by the clay from soil 3. Although the clay from this soil contains the smallest amount of montmorin, as indicated by x-ray and the electron microscope analyses, it nevertheless contains the highest amount of water.

The unusual aspect of these results is the presence of attapulgite in five of the six soils studied. It ranges from 8 to 80 per cent of the clay mineral content. The terra rossa soil, soil 2, is the only one which does not contain attapulgite. It is also important to note (*a*) that these soils represent both the North of Israel—profile 6—and the Center—profiles 1, 3, 5—all of which are derived directly from the underlying limestone, and (*b*) that the loess soil—profile 4—which is not derived directly from an underlying limestone rock, nevertheless has an attapulgite content equivalent to that of the soils derived directly from the limestone.

The clay mineral of greatest abundance in five of the six soil clays is montmorin. In these soils it ranges from 50 to 78 per cent of the clay mineral content. The clay from soil 3 is the exception—attapulgite, as mentioned previously, is the most abundant clay mineral.

Only in two of the six soil clays is kaolin present in appreciable quantities. These are soil 2—the terra rossa—and soil 5 –Eshtaol—namely, 35 and 25 per cent respectively. But on the basis of the natural state of the clays, only the terra rossa soil may be said to contain appreciable amounts of kaolin.

Inspection of the composition of the parent material residue (table 6) leaves no doubt that this residue represents the source of the clay minerals of the soil clays. There is, however, a definite change in the relative abundance, in the morphology, and in the cation-exchange capacity of the clay minerals during their transition from the source to the soil. These changes are as follows: In abundance, there is a definite decrease of attapulgite and a corresponding increase in montmorin, particularly in soil 1; there is also an increase in the kaolin content. In the morphology, the change is again marked most strongly in attapulgite: the particle size, measured both in length and in thickness, decreases severalfold. Kaolin, too, shows a definite change; it, too, decreases in particle size, and the sharp corners of the hexagonal plates of the particles become rounded. The change in montmorin, however, is difficult to judge, except perhaps in showing a decrease in particle size. In the cation-exchange capacity, the change is recorded by an increase in nearly all of the clay samples. Of particular interest is the large increase in the exchange capacity of the clay sample of soil 3, which consists mainly of attapulgite. It would appear that the exchange capacity of soil attapulgite is much higher than of attapulgite in clay deposits. The former appears to have a value of about 40 to 50 me. per 100 g., whereas the latter has been shown to have a capacity of about 7 to 20 (6, 9).

Particle size distribution. The particle size distribution is shown in table 7. In all but the loess profile, soil 4, the textures are heavy; this is particularly true in the soils of profile 2, the terra rossa. In this soil nearly all of the sand fraction is gone. In all of the profiles, except 1, there is a definite increase in the clay

TABLE 7

Mechanical analysis, surface color, and pH of six Israeli limestone soils

Sample	Total Sands, 2–0.05 mm.	Silt, 0.05–0.002 mm.	Clay		Surface Color*	pH
			<0.002 mm.	<0.001 mm.		
	%	%	%	%		
1a	20.9	35.9	43.2	41.5	Dark gray-brown	7.4
1b	17.0	43.0	40.0	27.5		
1c	18.5	33.9	47.6	37.0		
2a	1.8	24.7	73.5	68.3	Dark reddish brown	6.9
2b	1.3	20.0	78.7	73.5		
2c	1.2	18.8	80.0	76.0		
3a	12.5	45.9	41.6	22.3	Very pale brown	7.5
3b	11.0	47.2	41.8	30.0		
3c	12.0	41.3	46.7	37.0		
3d	13.5	40.0	46.5	37.2		
4a	46.0	34.2	19.8	13.0.	Light yellowish brown	7.5
4b	43.5	39.0	17.5	12.4		
4c	35.6	39.2	25.2	22.0		
4d	40.0	33.9	26.1	22.0		
5a	21.6	36.9	41.5	30.9	Grayish brown	7.5
5b	18.8	37.2	44.0	32.0		
6a	21.3	43.5	35.2	23.7	Light brownish gray	7.5
6b	22.0	35.1	42.9	38.6		

* Munsel colors.

fractions with depth. This increase is believed to result mainly from an increase in the carbonate content of colloidal dimension rather than from clay migration. The increase in carbonate content in the clay size dimension with increase in depth of profile is shown by the differential thermal analyses. It would appear, therefore, that at the surfaces the clay size carbonates weather at a faster rate than at greater depths. The change in color from darker to lighter shades, due to a decrease in organic matter, with increasing depth in the profiles appears to be the only other property to designate profile differentiation.

DISCUSSION

The importance of determining the nature and amount of the clay minerals in soils for a better understanding of the formation of soils and their correlation

is demonstrated by the results obtained in the present study. Thus it was shown that the clay minerals in soils derived from limestone are a mere reflection of those found in the acid-insoluble residue of the parent material. This was most strikingly demonstrated by the presence of attapulgite, which in a true sense served as an index to designate the transition of the limestone to soil and to show the relationship among the various limestone soils studied. Thus on the basis of the occurrence of attapulgite in the limestone, the samples studied fall into two distinct groups: one in which attapulgite is present, namely, the limestone from samples 1, 3, 5, and 6, and the other in which attapulgite is absent, namely, sample 2. It is noteworthy that the latter sample differs from the former samples in four other respects: first, it contains a larger proportion of $MgCO_3$; second, it is much harder and denser; third, it contains a much larger proportion of acid-soluble sesquioxides in relation to the acid-insoluble residue (table 4); and fourth, the amount of acid-insoluble residue is much smaller than in the other samples. Obviously the absence of attapulgite in the soil clay of sample 2—the terra rossa —is due to its absence in the parent rock, but whether the other differences noted in the nature of the clay minerals of this sample, namely, absence of lime and the larger amounts of kaolin and uncombined iron oxide, are the result of the differences in the nature of the limestone is discussed later.

The relatively small changes that occurred in the clay minerals during the transition from the parent rock to the soil material clearly indicate that the chief process involved in soil formation from limestone is removal by solution of the carbonates and accumulation of the residue. This apparently is true even in the terra rossa, from which all of the lime has disappeared but in which the base status is still very high, as indicated by its neutral pH. The presence of the larger amounts of free iron oxide in this sample, as indicated by its color, is also apparently a reflection of the nature of the parent material as shown by the high ratio of acid-soluble sesquioxides to the acid-insoluble residue—the source of the clay minerals. On the basis of these results, therefore, it seems unnecessary to invoke any special theory (18) to explain the presence of relatively larger amounts of iron oxide or aluminum oxide in proportion to the clay minerals in the terra rossa soils as contrasted with the other limestone soils. It is merely a reflection of the parent material The complete disappearance of the lime, however, may be due either to greater solubility of this particular hard limestone or to greater age of the soil. That time must be an important factor in the formation of the terra rossa is indicated by the fact that although the total content of insoluble residue together with acid-soluble sesquioxides and silica is extremely low—0.53 per cent—the amount of soil found, as measured by the thickness of the lime-free profile and the clay content, is very high. Such a condition seemingly could result only from a prolonged period of weathering.

The occurrence of montmorin as the most abundant clay mineral in all of the limestone soils studied, except one—sample 3—is in agreement with the findings of others (13), namely, that the presence of lime in a parent material either enhances the formation of the montmorin clay minerals or preserves them if they are originally present.

The problem of the formation of attapulgite in the limestone residue itself is of interest, but the present study sheds no light on it. Attapulgite definitely is not a product of soil formation; however, apparently weathers to montmorin and possibly also to kaolin type minerals.

The present study indirectly sheds light on the problem of the source of the parent material of the loess soils of southern Israel—the Negev. The similarity in attapulgite and montmorin contents between the soil clays from the loessal profile and those derived directly from the limestone soils indicates beyond any doubt that the parent material of this soil must have been derived from a limestone soil. This conclusion receives added weight from the fact that the presence of attapulgite heretofore has been demonstrated only in limestone or soils derived from limestone.

SUMMARY

The mineralogical and chemical compositions of the clay fractions from six Israeli soils derived from limestone and of the limestone itself were determined with particular attention to the nature of the clay minerals present. X-ray, differential and integral thermal, electron microscope, cation exchange, and total chemical analyses were made.

One of the most significant findings was the presence of the clay mineral attapulgite as a major constituent of five of the soils studied. Its presence was attributed to the acid-insoluble residue of the limestone parent materials, of which it is a major constituent.

The montmorin clay minerals were found to be the most abundant of the clay minerals in five of the soils, whereas attapulgite was the most abundant in one of them.

The kaolin clay minerals were found in only minor amounts in all but two soils. In all but one soil—the terra rossa—calcite was found to be one of the most abundant constituents of the clay fractions, and generally it increased in abundance with increasing depth in the profiles.

Quartz and mica-clay in small amounts were also present in all the soil clays.

All of the constituents of the soil clay fractions were inherited from the acid-insoluble residue of the limestone parent materials.

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ROLE OF SOLID PHASE IN PHOSPHORUS NUTRITION OF PLANTS AS REVEALED BY RADIOACTIVE INDICATOR

M. A. ISLAM

Agricultural Research Laboratory, Dacca, East Pakistan[1]

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A previous paper (2) presented evidence of the possible utilization of absorbed phosphorus on Aiken clay loam. The present paper offers additional evidence of this possibility and reports results of the use of radioactive phosphorus P32. By the use of radioactive K and Na with barley plants, Jenny, Overstreet, and Ayers (3) demonstrated that plants lose their cations when in direct contact with colloidal clay of low base saturation, a phenomenon they termed contact depletion. And by the use of radioactive sodium, Overstreet and Jenny (5) found that the relative absorption of sodium by barley roots from a large volume of Na-Yolo suspension was much higher than from large volumes of corresponding CO_2-saturated intermicellar liquid. These data were interpreted as strong evidence in support of the theory of contact exchange of cations. As for the anions, these investigators found that depletion of bromide does not occur in contact with suspensions of negative particles, but only in contact with an electrodialyzed iron hydroxide solution.

PROCEDURE

Approximately 1 kg. of Aiken soil was dispersed by means of an electric stirrer attached to a large crock. Particles less than 1 μ in diameter were separated by siphoning off the top 10 cm. of the suspension after a settling period of 24 hours. The suspension was concentrated by filtering it through Pasteur-Chamberlain candles with the aid of suction until a sufficient amount of clay was collected. A hydrogen colloid of this clay was then prepared in a Bradfield-type three-chambered electrodialysis cell. The electrodialyzed colloid had a pH of 5.2 and a much higher phosphate-fixing capacity than the original soil or the nonelectrodialyzed colloids.

A 0.4 per cent suspension of this colloid was prepared and radioactive phosphorus (P32) from a stock solution added to it. The suspension was stirred thoroughly, and after standing for 12 hours a small portion was centrifuged for 2 hours in a spinning-top type centrifuge to separate out the supernatant liquid. A 25-ml. aliquot of the supernatant liquid was evaporated to dryness. One-milliliter samples of the suspension were also similarly evaporated to dryness. After background correction, counts were taken for the radioactive phosphorus in the suspension and the supernatant liquid with a Geiger-Mueller counter. Then an artificial intermicellar liquid was prepared with the same counts of radioactive phosphorus as the supernatant liquid of the suspension.

[1] This work was carried out at the University of California under the guidance of Professor Hans Jenny, to whom the author expresses his gratitude.

TABLE 1

Contact absorption of radioactive phosphorus P32, by lettuce seedlings

System	Condition of Intermicellar Liquid	Oven-Dry Weight		Counts per Second		Counts per 10 mg.	
		Tops	Roots	Tops	Roots	Tops	Roots
		g.	g.				
1. 1 l. 0.4% clay suspension with 54.11 counts/sec./ml.; lettuce plants grown 42 hours	Av. counts in 25 ml. = 1.93	.0269	.0082	4.68	31.25	1.74	38.12
		.0248	.0080	3.92	31.18	1.58	38.98
		.0216	.0048	4.68	14.81	2.17	30.87
		.0248	.0062	6.34	13.48	2.56	21.74
		.0278	.0059	5.91	12.51	2.16	21.19
		.0246	.0059	5.92	13.58	2.41	28.97
2. Same as system 1 plus 5 mg. carrier P_2O_5	Av. counts in ml. = 6.4 Ordinary P_2O_5 in soln. = 0.0235 mg./l.	.0232	.0048	148.9	90.56	64.16	188.7
		.0290	.0080	348.9	149.9	120.3	187.4
		.0157	.0054	150.8	82.87	95.98	153.5
		.0233	.0060	231.2	113.9	99.86	189.7
		.0186	.0045	217.8	102.7	117.1	228.0
		.0189	.0052	159.6	91.61	84.45	176.2
3. Same as system 1 plus 10 mg. carrier P_2O_5	Av. counts in 25 ml. = 13.6 P_2O_5 in soln. = 0.1008 mg./l.	.0176	.0042	253.7	66.35	144.2	158.0
		.0197	.0044	361.8	71.32	183.7	162.1
		.0184	.0040	327.9	71.20	178.2	178.0
		.0167	.0037	316.3	63.87	189.3	172.6
		.0265	.0067	610.3	122.9	230.3	183.3
		.0261	.0068	519.2	131.9	189.0	193.9
4. 2 l. artificial intermicellar liquid corresponding to system 2; 500 counts 0.047 mg. P_2O_5	Same as in system 2	.0307	.0074	5.79	18.37	1.887	24.82
		.0351	.0088	3.07	19.23	0.875	21.85
		.0243	.0046	3.80	10.45	1.564	22.72
		.0191	.0040	7.52	8.44	3.938	21.10
		.0188	.0053	5.53	11.46	2.943	21.62
		.0261	.0077	3.66	17.78	1.403	23.63
5. 2 l. artificial intermicellar liquid corresponding to system 3; 1092.8 counts 0.2016 mg. P_2O_5	Same as in system 3	.0122	.0051	68.02	58.32	55.75	114.3
		.0306	.0082	124.3	86.19	40.53	105.2
		.0298	.0070	96.49	68.62	32.39	98.02
		.0294	.0068	98.83	64.88	33.62	99.08
		.0191	.0024	47.38	29.10	24.80	121.0
		.0197	.0057	71.94	53.71	23.03	98.87

Lettuce seedlings, after germination in the seedbed, were transferred in corks to a tank containing Hoagland solution without phosphorus, where they were allowed to grow for a few days to render them phosphorus-starved. Some were then placed in a 0.4 per cent suspension of Aiken clay treated with radioactive phosphorus and others in the corresponding artificial intermicellar liquid. Aeration was provided in all systems.

After 42 hours the plants were withdrawn from the systems, washed thoroughly

under running water, separated into roots and tops, oven-dried, and crushed. Counts were then taken separately for each sample (table 1).

RESULTS

Preliminary experiments showed that though the number of counts per milliliter of suspension was high, the number in the supernatant liquid was extremely small; during the period of experimentation the counts in the artificial intermicellar liquid became too low for accurate determination. System 1 (table 1) shows that at the start of the experiment the average number of counts per 25 ml. of the supernatant was only 1.93. At the end of the experiment the number of counts had been reduced to the level of background count (1.4 ± 0.08).

If some carrier phosphorus is added to the system, the number of counts in the intermicellar liquid will increase, and the degree of colloid phosphorus saturation will thereby also be increased. Thus more phosphorus becomes available for plant absorption and the presence of phosphorus, both radioactive and ordinary, in the intermicellar liquid is ensured. Systems 2 and 3 (table 1) were prepared by adding some carrier phosphorus, and systems 4 and 5 were artificial intermicellar liquids corresponding to the liquid phases of systems 2 and 3. The data (table 1) show that plants received more counts from the suspension than from the artificial intermicellar liquid.

As far as possible, uniform plants were used in the experiment and sufficient replication was provided. Counts taken for each sample of roots and tops have been expressed on the same weight basis and replications agree fairly closely in all the treatments. Enough radioactive and ordinary phosphorus remained in the artificial intermicellar liquid after the experiment to make it impossible for the exhaustion of isotopes from the liquid to be caused by the low absorption of that liquid. Moreover, in comparison to 1 liter of suspension, 2 liters of solution were provided for a given number of plants. These data corroborate the previously published results (2) on possible utilization of absorbed phosphorus.

Further, systems 1, 2, and 3 show that when the amount of carrier phosphorus was increased, the counts for the radioactive phosphorus in the plants was also increased, though the counts per milliliter of the suspension remained the same for each system. This demonstrates the importance of the degree of saturation, for by increasing the degree of saturation not only is the possibility of contact increased, but the ease of replacement is also increased. For practical agriculture this means that after the application of phosphatic fertilizer to a soil, though no phosphorus can be extracted by ordinary solvents, the beneficial effect of the application will not be lost. Since fertilization will increase the degree of saturation of the colloid with respect to phosphorus and will increase contact possibility, fertilization thus promotes better absorption.

The importance of the degree of saturation has been realized also by other workers (4). Burd and Murphy (1) demonstrated the correlation between plant growth and the degree of saturation of the soil with respect to phosphorus. Their suggestion that the degree of saturation helps to bring more phosphorus into solution is correct, but it is emphasized here that contact phenomenon also

plays an important part. In some cases both act together; in others, either contact or solution plays the dominant role. With Aiken soil, for example, under experimental conditions it is contact that appears to play the more dominant role with absorption from solution of minor importance. Contact absorption is important when the degree of saturation of the colloid is fairly high and the amount of phosphorus in the solution very low. On the other hand, when large amounts of phosphorus are in the solution, contact absorption will be difficult to detect and may play a minor role. According to Overstreet (6), contact absorption and suspension effects are manifestations of the same general phenomenon; thermodynamically he has shown that contact absorption will prevail when the amounts of nutrients in the intermicellar liquid are extremely small.

SUMMARY

Lettuce seedlings were grown in 0.4 per cent suspension of electrodialyzed Aiken colloid less than 1 μ in diameter and treated with radioactive phosphorus P32; others were grown in an artificial intermicellar liquid of the same concentration of radioactive and ordinary phosphorus as the liquid phase of the suspension. It was found that the number of counts for the radioactive phosphorus was higher in plants in the suspension than in those in the artificial intermicellar liquid. This indicates the possible plant utilization of phosphorus adsorbed on the soil colloids. Since the number of counts of radioactive phosphorus per milliliter of suspension remains unaltered, it appears that the absorption of radioactive phosphorus by plants is increased by increasing the amounts of carrier phosphorus, and that thus the absorption of adsorbed phosphorus by plants is increased by increasing the degree of saturation of the colloid with respect to phosphorus.

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INFLUENCE OF NITROGEN FERTILIZATION AND PLANT POPULATION DENSITY ON EVAPOTRANSPIRATION BY SUDAN GRASS

H. A. WEAVER AND R. W. PEARSON

U. S. Department of Agriculture[1]

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Evapotranspiration rates of agricultural crops are generally regarded as dependent on such factors as incident sunlight energy, wind velocity, relative humidity, air and soil temperature, crop species, and soil water availability. Certain combinations of these factors have been included in empirical formulas proposed by Blaney and Criddle (1), Penman (7), and Thornthwaite (8).

More recently reported data (3, 5) show that, in addition to these factors, fertility level can have a marked influence on the efficiency of use of water by crops, and other studies (2, 6) have indicated that transpiration varies considerably with physiological stage of development. No clear-cut effect of plant population or fertility level on total evapotranspiration has been shown, although van Bavel and Wilson (9) have suggested that plant stand is not a factor, provided there are sufficient plants to form a closed cover.

The present study was set up to determine the effects of soil nitrogen and plant population density levels on evapotranspiration by Sudan grass. Sudan grass was selected chiefly because of its known sensitivity to soil nitrogen variation and its characteristic of rapid growth. It is recognized that the conditions of this study with respect to the size of plot borders were not optimum for accurate determination of absolute values of evapotranspiration. Since, however, emphasis was being placed upon the effect of plant population and nitrogen fertilization levels on evapotranspiration rather than on the amounts of water lost *per se*, and the area available did not permit use of larger plots, some compromise on this question was accepted.

PROCEDURE

The experiment was of split plot design and consisted of eight main plots. Four of these plots were irrigated whenever the soil moisture tension at an 8-inch depth reached ½ atmosphere. The remaining four plots received no water other than rainfall except when damage from wilting was likely. Each main plot contained six randomly placed subplots representing three population density levels at each of two soil nitrogen levels. The soil moisture variable was introduced so that effects of density and nitrogen could be observed under both adequate and less favorable moisture conditions.

The experiment was conducted on the Lloyd clay bin of the U. S. Department of Agriculture Tillage Machinery Laboratory at Auburn, Alabama. Soil texture

[1] Contribution from the Soil and Water Conservation Research Branch and Tillage Machinery Laboratory, Agricultural Research Service, in cooperation with the Agricultural Experiment Station of the Alabama Polytechnic Institute.

was uniform to an 18-inch depth but was varied below that point as required by the drainage system used (4). The bin was 20 feet wide by 250 feet long and was surrounded by a concrete wall that projected about 4 inches above the soil surface. Subplots were 14 feet long and contained 7 rows 8 inches apart.

The Sudan grass was planted May 22 after an application of 400 pounds of 0-14-12 fertilizer per acre beneath the rows. After the grass had completely emerged, 100 pounds N per acre in the form of ammonium nitrate was applied to all plots designated for high nitrogen treatment. The remaining plots received no additional nitrogen. Stands were thinned to population densities of 44,000, 132,000, and 396,000 plants per acre.

Evapotranspiration measurements were begun on July 3, 1952, after the grass on all plots had been mowed to a 2-inch height. The measurements were continued until July 30, when the plants were in the soft dough stage. Soil moisture samples were taken at the beginning and end of each of four 6- to 7-day periods from each of three depths in each subplot. Depths selected were 0 to 6, 6 to 12, and 12 to 18 inches so that a measure of water depletion from the upper 18-inch soil layer was obtained. The difference between the quantity of water in the soil at the beginning and at the end of each successive period plus that added as irrigation and rainfall was assumed to be equal to evapotranspiration. This was a valid assumption in the study, because no runoff or percolation occurred. Although no provision was made for measurement of deep percolation losses, tensiometers were installed at a 17-inch depth to detect and permit isolation of periods of such loss. Fortunately, total rainfall for the 1 month duration of the experiment was only 1.03 inches.

A weather record was kept that included observations at 2- to 3-day intervals of wind mileage, relative incident sunlight energy, evaporation from a free water surface, and evaporation from an atmometer. Sunlight energy measurements were made with an electronic sunlight integrator. This instrument records the total number of discharges of an RC circuit whose rate of charge is directly related to the energy of the sunlight falling on a phototube. Although the instrument can be calibrated against a pyroheliometer to read in absolute energy terms, in this experiment only relative intensities were used since it was impossible to check the calibration at the end of the study. Complete records of precipitation, relative humidity, and temperature were made with recording instruments. The weather-sensitive element of each instrument was located at a 3-foot height above the soil surface in an adjacent bin.

RESULTS AND DISCUSSION

Variations in soil moisture contained in the 0- to 18-inch layer over the 27-day period are shown graphically in figure 1. These graphs represent the average conditions found at each of the two soil moisture levels. They show that the experiment was started with a deficiency of moisture at both levels, which would reduce evapotranspiration to less than potential. Moisture contents were gradually increased, however, during the first period to the extent that averages of 50 and 25 per cent of the available capacity were maintained for the high and low levels, respectively, throughout the remainder of the experiment.

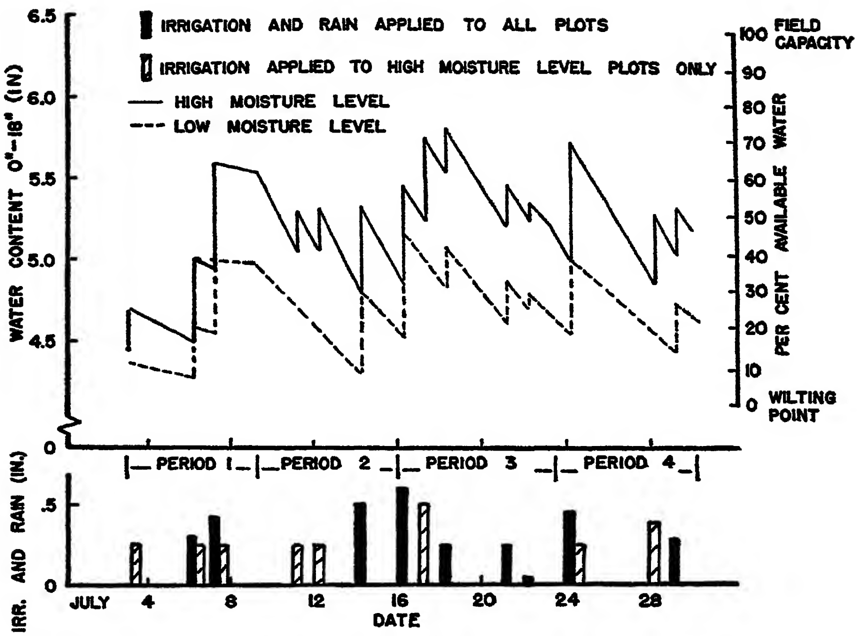

FIG. 1. Average Water Content of the 0- to 18-Inch Soil Layer for Sudan Grass Under Low and High Moisture Treatments During July 3–30

Average daily evapotranspiration rates for each of the four 6- to 7-day periods are given in table 1. The statistical evaluation of these data is given in table 2.

The effects of nitrogen, population density, and soil moisture level on evapotranspiration rates during the four periods are shown graphically in figures 2 and 3. Soil moisture level was the major factor limiting evapotranspiration in all periods, with maximum rate occurring always at the higher level of soil moisture. This is in agreement with the results of other studies (4). Figure 2 shows that addition of nitrogen was accompanied by small evapotranspiration increases during the second and third periods at the high level of soil moisture. These increases averaged approximately 7 per cent. There was no effect of nitrogen, however, during any period at the low level of soil moisture. The effect of population density (fig. 3) was appreciable in the third period. Evapotranspiration was highest for the intermediate population at both moisture levels. Rates averaged 39 per cent higher than those for other populations at the upper level of soil moisture and 36 per cent higher at the lower level. There is no readily apparent reason for this effect. There was little difference due to population density in the other periods.

Evapotranspiration was affected to some degree by stage of growth. Figures 2 and 3 show a marked increase between the first and second periods followed by a definite decline in rate between the last two periods. The effect of stage of growth was confused to some extent, however, by soil moisture availability and changes in weather factors (see open pan and atmometer evaporation rates, table 5).

TABLE 1

Evapotranspiration by Sudan grass by periods and treatments

Average inches daily

Date	Evapotranspiration by Sudan Grass*					
	D_1N_1	D_2N_1	D_3N_1	D_1N_2	D_2N_2	D_3N_2
	High soil moisture					
July 3–9...	.075	.100	.072	.080	.075	.060
July 9–16..	.248	.228	.218	.237	.231	.247
July 16–23..	.169	.246	.180	.203	.277	.193
July 23–30..	.230	.201	.177	.206	.210	.198
	Low soil moisture					
July 3–9...	.040	.012	−.002	.027	.037	.007
July 9–16..	.126	.130	.156	.133	.123	.139
July 16–23..	.151	.196	.129	.146	.190	.141
July 23–30..	.111	.107	.114	.107	.104	.109

* D_1 = 44,000 plants per acre; D_2 = 132,000 plants per acre; D_3 = 396,000 plants per acre; N_1 = no nitrogen applied; N_2 = 100 pounds N applied per acre.

TABLE 2

Statistical evaluation of evapotranspiration data of table 1

Source of Variation	Probability of Variation Due to Chance			
	July 3–9	July 9–16	July 16–23	July 23–30
Soil moisture levels	<.005**	<.005**	<.005**	<.005**
Soil nitrogen levels	>.10	>.10	<.025*	>.10
Population density levels	>.10	>.10	<.005** (quadratic)	>.10
Nitrogen × population interaction	>.10	>.10	<.10	>.10
Nitrogen × moisture interaction	>.10	<.10	<.025*	>.10
Population × moisture interaction	>.10	<.05* (linear)	<.05* (quadratic)	<.01** (linear)
Nitrogen × population × moisture interaction	>.10	<.005** (linear)	>.10	<.10 (linear)

* Significant at 5 per cent level.
** Significant at 1 per cent level.

A depressing effect of maturity on evapotranspiration in the fourth period was evident, however, particularly at the low level of soil moisture, notwithstanding relatively dry atmospheric conditions.

Values of total evapotranspiration for the 27-day growing period are given in table 3. The corresponding statistical data are presented in table 4. A significantly higher total use of water at the intermediate population than at others reflected the high rate of use previously noted for the third period.

A small though significant nitrogen × population interaction also occurred,

wherein nitrogen had no appreciable effect on evapotranspiration at the low and intermediate population levels but induced an increase of approximately 7 per cent at the upper level.

No consistent trends existed to suggest that the quantity of plant material produced was a major factor in controlling total evapotranspiration losses. Where large increases in total dry matter (see table 3) resulted from increased soil moisture availability, the attendant increases in total evapotranspiration may have been due to more normal stomatal activity and greater evaporation

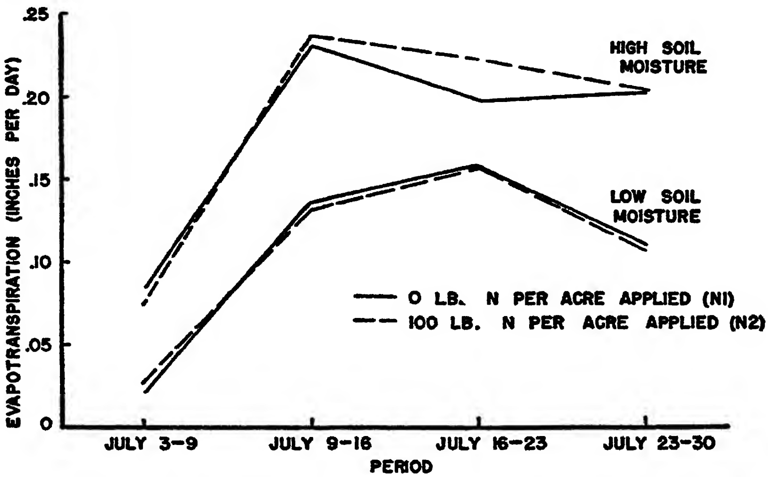

FIG. 2. Effect of Application of 100 Pounds Nitrogen per Acre on Daily Evapotranspiration Rates of Sudan Grass at Two Levels of Soil Moisture

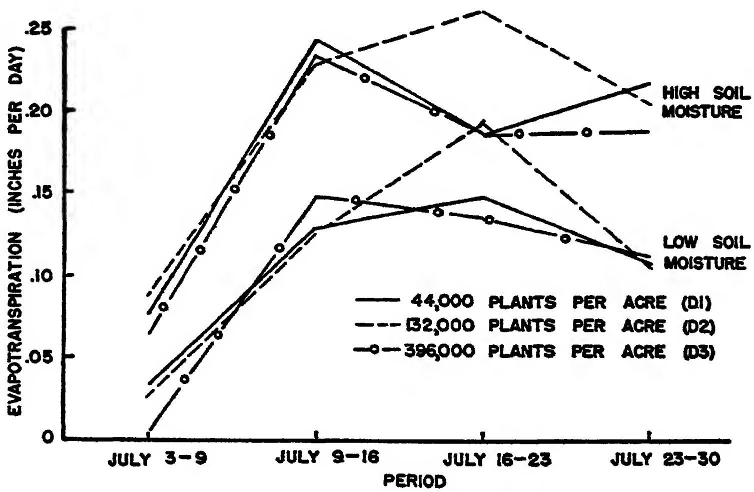

FIG. 3 Effect of Population Density on Evapotranspiration Rates of Sudan Grass at Two Levels of Soil Moisture

losses from the soil surface, since the large growth increases effected by nitrogen did not induce any over-all significant change in total water loss.

The maximum effect of treatment on evapotranspiration at the upper moisture level was one in which total water use for the intermediate population × high

TABLE 3

Total Sudan grass evapotranspiration, dry matter produced, and ratios of evapotranspiration to dry matter for six treatments at each of two levels of soil moisture for July 3–30

Subtreatment*	High Soil Moisture			Low Soil Moisture		
	E†	Dry Matter‡	E/D.M.§	E	Dry Matter	E/D.M.
	in.	*lb./A.*	*lb./lb.*	*in.*	*lb./A.*	*lb./lb.*
D_1N_1	4.97	1,792	639	2.96	1,018	665
D_2N_1	5.32	1,993	628	3.09	1,024	712
D_3N_1	4.45	1,590	648	2.78	1,454	460
N_1(Av.)	4.91	1,791	638	2.94	1,165	612
D_1N_2	4.98	2,804	403	2.86	1,481	445
D_2N_2	5.49	3,376	374	3.04	1,644	483
D_3N_2	4.83	3,087	357	2.96	1,846	367
N_2(Av.)	5.10	3,089	378	2.95	1,657	432

* D_1 = 44,000 plants per acre; D_2 = 132,000 plants per acre; D_3 = 396,000 plants per acre; N_1 = no nitrogen applied; N_2 = 100 lb. N applied per acre.

† E = evapotranspiration, average of four trials.

‡ Average of four trials.

§ $\frac{\text{E}}{\text{D.M.}} = \frac{\text{evapotranspiration (lb./A.)}}{\text{dry matter produced (lb./A.)}}$, average of four trials.

TABLE 4

Statistical evaluation of the data of table 3

Source of Variation	Probability of Variation Due to Chance		
	E†	$\frac{\text{E}}{\text{D.M.}}$‡	Dry Matter Production
Soil moisture levels	<.005**	>.10	<.005**
Soil nitrogen levels	<.10	<.005**	<.005**
Population density levels	<.005** (quadratic)	<.05* (linear)	<.05* (linear)
Nitrogen × population interaction	<.05* (linear)	>.10	>.10
Nitrogen × moisture interaction	>.10	>.10	<.005**
Population × moisture interaction	<.005** (quadratic)	<.05* (quadratic)	<.025* (quadratic)
Nitrogen × population × moisture interaction	>.10	>.10	>.10

* Significant at 5 per cent level.

** Significant at 1 per cent level.

† Evapotranspiration.

‡ $\frac{\text{E}}{\text{D.M.}} = \frac{\text{evapotranspiration (lb./A.)}}{\text{dry matter produced (lb./A.)}}$.

TABLE 5

Weather data for the four periods of measurement of sudan grass evapotranspiration

Period	Mean Temperature	Average Relative Humidity	Wind	Sunlight*	Evaporation	
					Open pan	Atmometer
	°F.	%	*mi./day*	*units/day*	*in./day*	*ml./day*
July 3–9	75.9	79.1	†	429	.30	57
July 9–16	77.1	71.4	47	485	.37	62
July 16–23	82.3	71.9	48	441	.34	61
July 23–30	81.1	65.4	45	616	.42	82

* Determined by use of a sunlight integrator. Arbitrary units providing a relative indication of incident sunlight energy.

† Wind data not available for this period.

nitrogen treatment was 1.04 inches (23 per cent) higher than that for the high population × low nitrogen treatment. This difference was primarily the result of a consistently high total use by the intermediate population level. A difference of this magnitude emphasizes the need for considering management practice in the determination of irrigation schedules.

Water-use efficiency was calculated as the number of pounds of water required for the production of 1 pound of dry matter during the period July 3–30. These values for evapotranspiration–dry-matter ratio for each treatment are given in table 3, and the statistical evaluation is presented in table 4. The largest increases in efficiency were effected by nitrogen through stimulation of dry matter production without appreciable change in water requirement. Over-all average water use at the low nitrogen level was 625 pounds per pound of dry matter as compared with 405 pounds at the high nitrogen level.

The statistical analysis indicated an over-all linear increase in efficiency with population increase. This suggested that the thicker stands had a conserving effect, probably due to reduced air movement about the exposed plant and soil surfaces. The only deviation from linearity was that of a very low efficiency noted at the intermediate population where soil moisture was low. This deviation accounted for the population × moisture level interaction of table 4. It apparently resulted from the high third period water-use rate noted previously.

Weather data obtained during the experiment are summarized in table 5. These data were used in calculating evapotranspiration losses from the empirical formulas proposed by Blaney and Criddle, Thornthwaite, and Penman. The daily rates determined by these methods are listed in table 6 along with average actual evapotranspiration rates for the Sudan grass.

Application of the Blaney and Criddle $u = kf$ formula involved use of a consumptive-use coefficient, k, of 0.70 proposed for sorghum. The monthly rates, u, were calculated by use of mean temperatures for each 6- to 7-day period. These values of consumptive use were then converted to daily rates. Similarly the 6- to 7-day period mean temperatures were applied as monthly means to the Thornthwaite method, and the results were reduced to daily rates of potential evapotranspiration. Penman proposed, as an aerodynamic approach, a formula

TABLE 6

Actual and empirically determined evapotranspiration for the four sudan grass growing periods

Average inches per day

Date	Actual Evapotranspiration*		Computed Evapotranspiration		
	High soil moisture	Low soil moisture	Blaney and Criddle	Thornthwaite	Penman
July 3–9	.077	.020	.173	.175	†
July 9–16	.235	.135	.176	.194	.166
July 16–23	.211	.159	.187	.233	.187
July 23–30	.204	.109	.182	.227	.222
July 3–30	.182	.103	.179	.207	—

* Each value is the average for six subtreatments.

† Wind data not available for this period.

which involved both wind and humidity factors but which included no factor for the direct effects of temperature and light. Calculation of evaporation from a surface in which the supply of water is unrestricted was proposed as follows:

$$E = .0013\,P(1 - h)u^{0.76}$$

where E = inches evaporation per day; P = saturation vapor pressure at mean air temperature; h = relative humidity; u = miles of wind per day.

No substantial correlation was found in the present study between actual and computed evapotranspiration when considered by periods during the growth cycle, but the average of the computed values for the entire period of the experiment was very nearly the same as the average of the measured values where the soil moisture was not limiting. The actual values were smaller during the early stages of growth and larger during the later periods than the calculated rates. The value of the empirical formulas for determining periodic water requirements of a short-season crop as grown here is not substantiated by this study. Sharp actual differences such as those due to population in the third period indicate that weather and crop species factors do not alone determine evapotranspiration rates.

CONCLUSIONS

Evapotranspiration rates by Sudan grass grown in Lloyd clay at two levels of soil moisture, three levels of plant density, and two levels of nitrogen were observed for a 1-month period, during which the plants grew from a height of about 2 inches to maturity for hay.

Evapotranspiration rate was affected very little by nitrogen level, but it was influenced appreciably by plant population level. Water-use efficiency, however, was greatly increased by application of nitrogen, which produced a relatively heavy growth of grass without appreciable change in total evapotranspiration. An over-all linear increase in efficiency with population increase also occurred.

Evapotranspiration rates were appreciably greater for all treatments and periods at the high level of soil moisture than at the low level.

Minimum evapotranspiration for all treatments occurred during the first week, when water availability was relatively low for both levels of soil moisture, climatic factors favored low evaporation, and the plants were small. Maximum rates occurred during the second and third weeks, and a general decline took place in the fourth week, when plants entered the early dough stage.

Calculated evapotranspiration rates for the 6- to 7-day periods were not correlated with actual rates for this short-season crop. The calculated total values for the month, however, were about in line with actual values where soil moisture was not limiting.

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FIXATION OF NITROGEN BY ALGAE IN RICE SOILS

P. K. DE AND L. N. MANDAL

State Agricultural Research Institute, West Bengal, India

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Although some nitrogen-fixing blue-green algae have been isolated from rice soils, there is little information on the magnitude of nitrogen fixation brought about by these organisms in soils under rice-field conditions. De and Sulaiman (3) conducted an experiment in which rice plants were grown in pots for five successive years both in presence and in absence of algae. Analysis of these soils at the start and end of the experiment showed a gain of 30–40 ppm. of nitrogen in pots with algal growth, whereas those without algal growth showed a nitrogen loss. Watanabe, Nishigaki, and Konishi (9) observed a fixation corresponding to 20 pounds of nitrogen per acre of soil in pots cropped with rice plants and inoculated with *Tolypothrix tenuis*—a powerful nitrogen-fixing alga. Prasad (6) analyzed the thick algal deposit on the rice lands of South Bihar and concluded that 12.9 pounds nitrogen per acre is added to rice fields after harvest as a result of fixation by algae. Willis and Green (10) showed by a pot experiment that the amount of nitrogen that was fixed in the soil by blue-green algae was enough to support a good crop of rice and leave about 70 pounds per acre in the soil after the crop was harvested.

A fairly large proportion of nitrogen fixed by algae occurs as soluble extracellular compounds (2, 4), which when formed in waterlogged rice soils may be either lost in drainage water or utilized for plant growth. Sulaiman (7) reported that nitrogen is lost when the dried algal bodies from a rice field are allowed to decompose in the soil. An analysis of the soil, therefore, does not appear to account for the total amount of nitrogen fixed by algae. In addition, the high standard error of Kjeldahl's method of nitrogen determination and errors caused by soil heterogeneity make it almost impossible to estimate small additions of nitrogen to the soils by means of soil analysis. In the present investigation, nitrogen fixation was studied by analysis of the gases in the soil atmosphere, a method by which small changes in the volumes of different gases in the soil atmosphere could be followed with a fair degree of accuracy.

EXPERIMENTAL

Arrangement of the apparatus is shown in figure 1. The experimental unit was a 10-liter aspirator bottle provided with two rubber stoppers, one fitted to the bottom tubulure and the other, carrying three glass tubes, to the mouth. The central tube with a diameter of 1 inch, projected about 3 inches above and 6 inches below the stopper (for uncropped bottles the central tube was dispensed with). The other two tubes were bent at right angles; one was connected to a nitrometer and the other was kept closed by a pinchcock attached to a small rubber tube. This latter tube was used to obtain gas samples for analysis. To

each aspirator bottle was added 18 pounds of soil brought to waterlogged conditions by addition of sufficient water; different treatments were then applied, and rice seedlings were transplanted where necessary. The transplanted seedlings were allowed to pass through the central glass tube, the lower end of which was always kept under water (fig. 1). To control the temperature and reproduce the rice-field conditions as closely as possible, the bottles were placed in a large masonry tank filled with soil and water. By applying gentle pressure, each bottle was pushed into the soft soil layer in the tank until the soil in the bottle and that

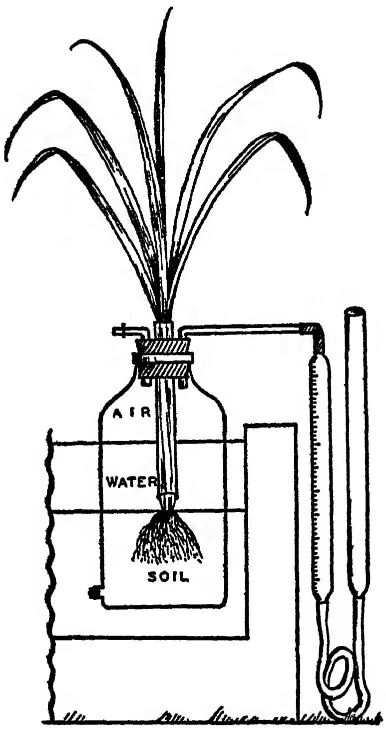

FIG. 1. APPARATUS FOR DETERMINING NITROGEN-FIXING CAPACITY OF BLUE-GREEN ALGAE

in the tank were at the same level. Similarly, the height of water in the tank was so adjusted that it remained at the same level as the water in the bottle.

Nitrogen fixed in each bottle was estimated at weekly intervals by analysis of the gas. For this purpose a measured volume of air (1300 ml.) was introduced at the start to each bottle by first filling the bottle with water and then withdrawing 1300 ml. of the water. The rubber stopper on the top, with the nitrometer tube completely filled with water, was then replaced. Throughout the experiment the gas in the bottle was maintained at nearly atmospheric pressure by lowering or raising the side tube attached to the nitrometer as required. At the end of each week, first a sample of gas was taken from each bottle for analysis, and then the rubber stopper on the top was slightly raised and the bottles were

TABLE 1

Results of soil analysis

Soil	Texture	pH	Total N	Exchangeable Calcium	Total P_2O_5	Available P_2O_5
			%	*me./100 g. CaO*	%	%
Chinsura	Clay	6.6	0.118	17.1	0.065	0.0095
Krishnagar	Sandy loam	7.0	0.065	2.63	0.132	0.0387
Kaity	Sandy loam	5.7	0.050	2.85	0.0248	0.0015
Uchalan	Sandy loam	5.8	0.048	4.83	0.0237	0.0023
Tollygunge	Silty loam	7.1	0.090	19.31	0.060	0.0097
Sonarpur	Clay	7.4	0.134	17.12	0.115	0.0277

filled by a careful addition of water. The volume of water thus added plus the volume of the gas removed for analysis and that remaining in the nitrometer gave the total volume of the gas formed in each bottle. After the analysis, 1300 ml. of water was again taken from each bottle and the whole process repeated as before. Since a large volume of water was lost by transpiration from the cropped bottles, water, when required, was added to these bottles through the central tube.

Six rice soils were used in this experiment. Table 1 shows the results of the soil analysis. The different treatments applied to the Chinsura and Krishnagar soils, which were studied in more detail than the rest, were as follows:

(*a*) No treatment (cropped).

(*b*) Superphosphate (1.1 g. added per bottle) corresponding to 60 pounds P_2O_5 per acre.

(*c*) Same as (*b*) plus $NaMoO_4$ solution at the rate of 4 ounces per acre.

(*d*) Same as (*c*), but with bottles wrapped to the neck with black paper to keep the soil and the supernatant water in the dark.

Similar sets of bottles without crop were run for the Krishnagar and the Chinsura soils. The other four soils received treatments (*a*) and (*b*), and no uncropped series of bottles were run.

There was very little visible growth of algae in the soil in the first week of the experiment, but in the second week, algae began to appear on the soil surface and also on the walls of the bottles. Growth was maximum in the third week, when algae floated on top of the water to form in some instances a thick layer. This floating growth, however, began to disintegrate in a few days and disappeared almost completely by the end of the fifth week. Phosphate stimulated algal growth in Chinsura, Kaity, and Uchalan soils, but no appreciable effect of molybdenum was observed in any instance. There was no visible growth of algae in any of the bottles kept in the dark.

Except in the bottles kept in the dark, volumes of gases found at the end of each week were much greater than at the start. This was due to the formation of a large volume of oxygen as a result of photosynthetic activity of algae and other aquatic organisms that appeared in the soil. Gases were analyzed according to the method described by Treadwell and Hall (8). The difference between the

total volume of nitrogen found at the end of the week and the volume of nitrogen contained in 1300 ml. of air (1033 ml.) represented the volume of nitrogen fixed.

The results of gas analysis (table 2) show that nitrogen fixation was greater in presence of a crop than in its absence. The application of phosphate stimulated both algal growth and nitrogen fixation in Chinsura, Kaity, and Uchalan soils. Analysis showed these soils to be comparatively poor in available phosphate (table 1). Bortels (1) and Fogg (5) showed that molybdenum is essential for the achievement of maximum rates of nitrogen fixation by blue-green algae. In the present experiment molybdenum stimulated nitrogen fixation in Chinsura soil, but its effect on Krishnagar soil was negligible. In the light, an abundant growth of algae took place in the soils, and nitrogen fixation was also fairly great. But in the dark, algal growth was absent, and not only was the amount of nitrogen fixed negligible, but nitrogen was lost from the Krishnagar soil. These results lend support to the view that fixation of nitrogen in waterlogged rice soils is an algal process.

TABLE 2

Total volumes of nitrogen fixed in each aspirator bottle

Volume at 32° C. and 760 mm. pressure

Soil	Duration of Experiment	N Fixed Under Different Treatments			
		Control	P_2O_5	P_2O_5 + Mo (in light)	P_2O_5 + Mo (in dark)
	wk.	*ml.*	*ml.*	*ml.*	*ml.*
Chinsura (cropped)	6	166.0	234.0	264.0	30.5
Chinsura (uncropped)	6	131.0	207.0	254.0	19.0
Krishnagar (cropped)	6	128.0	143.0	149.0	−9.7
Krishnagar (uncropped)	5	110.0	123.0	139.0	−23.6
Kaity (cropped)	5	81.0	148.0	—	—
Uchalan (cropped)	5	110.0	153.0	—	—
Tollygunge (cropped)	5	107.0	133.0	—	—
Sonarpur (cropped)	5	51.5	63.0	—	—

TABLE 3

Nitrogen fixation in different soils

Soil	N Fixed Under Different Treatments		
	Control	P_2O_5	P_2O_5 + Mo
	lb./A.	*lb./A.*	*lb./A.*
Chinsura (Cropped)	44.4	62.7	70.8
Chinsura (uncropped)	35.1	55.5	68.1
Krishnagar (cropped)	34.2	38.4	39.9
Krishnagar (uncropped)	29.4	33.0	37.2
Kaity (cropped)	21.6	39.6	—
Uchalan (cropped)	29.4	41.1	—
Tollygunge (cropped)	28.8	35.7	—
Sonarpur (cropped)	13.8	16.8	—

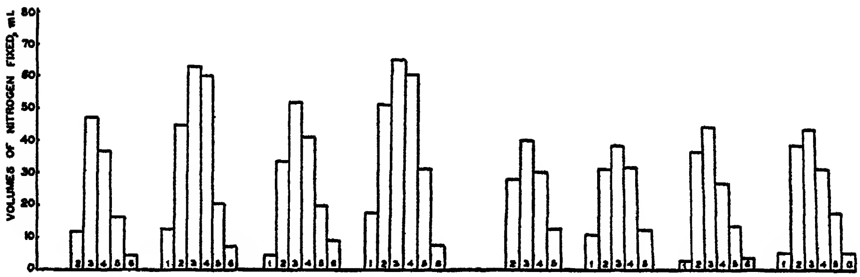

FIG. 2. VOLUMES OF NITROGEN FIXED IN DIFFERENT WEEKS

A, Chinsura soil, uncropped, no treatment; B, Chinsura soil, uncropped, treated with P_2O_5; C, Chinsura soil, cropped, no treatment; D, Chinsura soil, cropped, treated with P_2O_5; E, Krishnagar soil, uncropped, no treatment; F, Krishnagar soil, uncropped, treated with P_2O_5; G, Krishnagar soil, cropped, no treatment; H, Krishnagar soil, cropped, treated with P_2O_5. The weeks are numbered.

To obtain an idea of the amount of nitrogen added to the soil as a result of fixation by algae, the results in table 2 were calculated in terms of pounds per acre. Since algae are photosynthetic, their growth is restricted mostly to soil surface. The fixation of nitrogen in each bottle was assumed, therefore, to have taken place in an area of soil represented by the cross section of the bottle. The results thus calculated are shown in table 3.

The volumes of nitrogen fixed in successive weeks are shown in figure 2. In the first week the amount of nitrogen fixed was very small; in a few instances a loss of nitrogen was observed. In the second week fixation was fairly large; and in the third, maximum; in the fourth week the rate began to fall and the decline continued until in the sixth week fixation was almost negligible.

A comparison, at weekly intervals, of the volumes of nitrogen fixed with the volumes of oxygen evolved as a result of photosynthetic activity showed that there is no relationship between nitrogen fixation and photosynthesis. From Krishnagar soils large volumes of oxygen evolved in the first week of the experiment, but in the same period there was little fixation of nitrogen. And when, in the third week fixation was maximum, the rate of oxygen evolution had dropped to nearly half that of the second week. In the final week, oxygen evolution was nearly as great as in the third week, but nitrogen fixation was almost negligible. With Chinsura soil, the results were somewhat different. Fairly large volumes of oxygen evolved from these soils also in the first week when little nitrogen was fixed, but in the second and third weeks the rates of both nitrogen fixation and oxygen evolution were high. In the fourth week, however, there was a sharp fall in oxygen evolution while nitrogen fixation continued to be almost as high as before. In the final week, both nitrogen fixation and oxygen evolution were negligible.

Carbon dioxide evolved from the soils at a more or less uniform rate from the beginning of the experiment. Methane, however, could not be detected in the gas mixtures during the first 3 weeks of the experiment, but it did evolve from

Krishnagar soil without crop in the fourth week and from that with crop in the fifth week. From Chinsura soil without and with crop, methane was evolved in the fifth and sixth week, respectively.

SUMMARY

The amounts of nitrogen fixed by algae in six rice soils under waterlogged conditions were determined by weekly analyses of the gases in the soil atmosphere. In the cropped but unfertilized soils fixation varied from 13.8 to 44.4 pounds of nitrogen per acre. Application of superphosphate at the rate of 60 pounds of P_2O_5 per acre stimulated nitrogen fixation only in soils relatively poor in this nutrient. In certain soils there was evidence that application of molybdenum with phosphate might bring about greater fixation of nitrogen than did phosphate alone. More than 80 per cent of the fixation was shown to take place in the first 4 weeks after transplantation. Although there was considerable evolution of oxygen from the soils, no relationship could be established between the fixation of the nitrogen and the evolution of oxygen. Carbon dioxide evolved from the soils from the beginning of the experiment at an almost uniform rate, but methane could not be detected in the gas mixtures earlier than 3 or 4 weeks after transplantation.

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PERTINENT FACTORS GOVERNING THE AVAILABILITY OF SOIL MOISTURE TO PLANTS

VERNON C. JAMISON

United States Department of Agriculture[1]

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The soil and plant factors that govern moisture supply and availability to crops are of primary importance in crop production, and since the development of agricultural sciences began they have attracted the interest of both soil and plant scientists. The work reported is too voluminous to allow a comprehensive review here. Moreover, the subject has been thoroughly discussed by Kramer (45, pp. 18–72), Kelley (43), and Richards and Wadleigh (64, pp. 73–251). The present paper refers not only to these reviews but also to some very recent work and to selected published information that illustrate the points discussed.

Although soil and plant scientists for many years attributed the supply and availability of soil moisture to plants almost exclusively to soil properties, we now know that numerous plant and climatic factors are also involved. In a broader sense, the supply of available moisture to plants in a soil is the total quantity that can be extracted from the profile in the plant growth and maturing processes. The plant factors that affect the available moisture supply are (*a*) plant conditions (including nutrients present, stage of growth, degree of turgor), (*b*) rooting habit (including depth of rooting, degree of ramification, and absorptive activity), and (*c*) plant resistance to drought. Climatic factors are air temperature and air humidity (including the effect of fogs and wind). Soil factors are (*a*) moisture tension relations, (*b*) soil solution osmotic pressure effects, (*c*) kinds of ions present in the soil solution, (*d*) soil moisture conductivity, (*e*) soil depth, (*f*) soil stratification, including the effect of hardpans and textural layering, and (*g*) soil temperature and temperature gradients. In this paper, the plant and climatic factors are discussed very briefly, and the soil factors that affect available moisture storage capacity and efficiency are given some attention.

PLANT FACTORS THAT AFFECT AVAILABLE MOISTURE SUPPLY

The maximum available moisture content of any soil with unrestricted drainage is usually considered that held between its so called field capacity and its permanent wilting percentage. The field capacity is taken as a point or narrow range on the time drainage curve of a soil where the changes in moisture percentage occurring after thorough wetting with irrigation or rainwater become

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very slow. The so-called gravitational water that drains away rapidly after a well-drained soil is thoroughly wetted is usually considered of little consequence to plant growth. The permanent wilting percentage of a soil is taken as that moisture content at which plants first wilt without recovery in a humid atmosphere, unless water is added to the soil (76). The upper and lower limits of the available moisture percentage range are generally considered as soil characteristics. It should be emphasized that the quantity of available water that can be supplied depends also on several plant and climatic factors. Even though most plants wilt or stop growing at about the same moisture content of any one kind of soil in which they are rooted, the drought resistance of plants (43) varies widely. Guayule will withstand long periods of drought and renew growth when moisture is again available. Likewise, sorghum can be subjected to considerable moisture stress and will renew growth. On the other hand, such crops as celery, potatoes, and lettuce are very sensitive to drought. Plants probably vary over a range of several atmospheres in the suction force exerted *through* the roots on the moisture in the soil at the permanent wilting percentage. Furr and Reeve (23) found differences of 9 to 22 atmospheres osmotic pressure in the extracted sap of wilted plants. Since the turgor pressure of the plant cells is probably near zero at wilting, one may take the variation given as an indication of a wide range in soil moisture stress at wilting for the plants studied. Richards, Campbell, and Healton (63) found the soil moisture stress for sunflower and cotton at permanent wilting on 16 soils to range from 7 to 43 atmospheres. The wide change in moisture stress due to moisture tension alone for most soils near the wilting percentage is discussed in a later section.

Plants vary considerably in rooting habit, with regard to both depth and ramification (3, 6, 16, 24, 30, 32, 38, 43, 45, 50, 56, 57, 80). The quantities of water that different crop plants will extract from the same soil profile will vary widely with stage of growth (65) and kind of plant. Although the root extraction pattern of maturing plants depends largely on the kind of plant (30, 33, 45, 56) it can be modified by such variables as thickness of stand, soil aeration, soil fertility, dense soil layers, and a high water table (16, 19, 29, 43, 48, 49, 51, 56, 57, 68, 78, 80). Any factor that will affect the vigor or condition of a plant may be expected to influence the extraction of moisture from the soil. Kramer (46) found that wilting of sunflower plants reduced the rate of intake when water was again made available. Injury to plant roots through flooding may reduce absorption of water through plugging of conductive tissue (47) or reduction of absorptive surfaces. Crop management practices will affect soil moisture availability to the crop to be harvested. Rock and Lowe (67), found that available water stored during the summer for fall-planted wheat may be conserved for the production of grain by judicious winter pasturing.

CLIMATIC FACTORS THAT INFLUENCE MOISTURE SUPPLY

Ordinarily, loss of moisture from the soil surface is considered small in comparison with that transpiring from plants (12, 22). With sparse plant cover and over long periods (36, 37) loss by evaporation may be considerable. Soil evapora-

tion losses may be increased by soil-air temperature differences. On cold nights moisture vapor will move from warm moist subsoil layers and condense in the colder soil surface, where much of it may be lost by evaporation during the day, especially if the air is warm and dry and being changed by movement over the soil surface. Likewise, on warm days moisture vapor will move from the surface, where it would be available to shallow-rooted plants, and condense in the cooler subsoil. Gains or losses of available moisture due to evaporation and condensation are considered important under certain climatic conditions (7, 27). Under conditions of high humidity or fog, plants may absorb considerable moisture through leaf surfaces (8, 10) and continue to grow though the available moisture supply of the soil is limited. On the other hand, Henrici (35) has cited cases where plants wilted on hot, dry, windy days, even though the soil moisture supply was adequate. Likewise, plants often wilt during freezing weather. This has been attributed by Kramer (45, pp. 18–72) to damage to plant tissues and by Bethlahmy (4) to high moisture stress due to freezing of soil. The effect of climate on soil moisture supply is further indicated by the fact that the moisture storage needed to produce a good wheat crop increases with increasing average daily summer temperature as one moves from north to south over the wheat belt. Because of increase in transpiration rate of plants with increase in air temperature, and hence lowered relative humidity, the water requirement of plants increases. In general, the same moisture supply in North Dakota and Texas will produce more plant dry matter in North Dakota. Some soil moisture tension and conductivity factors modify this effect.

SOIL FACTORS THAT AFFECT MOISTURE AVAILABILITY

As water is withdrawn from the soil and the moisture content progressively decreases from field capacity to the permanent wilting percentage, there is a progressive increase in the forces resisting withdrawal, referred to as soil moisture stress (64, 77). Soil moisture stress has two components, soil moisture tension and osmotic pressure in the soil solution. The moisture tension component varies with the effective curvature of air-water surfaces in the soil. For most soils the approximate tension at field capacity varies between 0.2 and 0.5 atmosphere, depending on soil texture, compaction, stratification, depth of wetting, and other factors (14, 20, 31, 37, 43, 55, 61, 66, 69). For most soils of low salt content the moisture tension near the permanent wilting percentage is approximately 15 atmospheres (58), though wide variations with different soil-plant couples are evident (63). To understand some of the reasons for variations with tension for both the field capacity and the permanent wilting percentage, one should consider some moisture tension relationships for soils of different textures.

Figure 1 shows moisture release curves for four different soil samples, Lakeland sand, Hiwassee sandy loam, Commerce silt loam, and Sharkey clay. Generally, more water is withdrawn with tension increase at low tensions near field capacity than as the wilting range is approached. This is especially true for coarse textured sandy soils. The sandy soils lose most of their available moisture below 1 atmosphere tension, and silt loam and clay, below about 4 atmospheres.

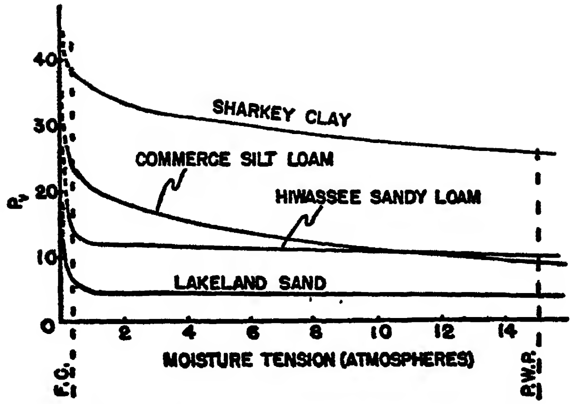

FIG. 1. VOLUME PERCENTAGE MOISTURE FOR SEVERAL SOILS OVER THE AVAILABLE MOISTURE RANGE FROM FIELD CAPACITY TO PERMANENT WILTING PERCENTAGE

P_v, volume percentage moisture; F. C., field capacity, taken as ⅓ atmosphere; P. W. P., permanent wilting percentage, taken as 15 atmospheres

There is no evidence of sharp breaks or discontinuities near the approximate field capacity or the permanent wilting percentage. The tension can change several atmospheres in the wilting range with little change in moisture content.

Colman (14) defined field capacity as a point on the soil profile drainage curve where the rate of moisture change is slower than earlier rates. Others have shown it is not an equilibrium condition (20, 37, 54, 55, 66, 76). The rate of movement of moisture in an unsaturated soil depends on two variables, the driving force (the hydraulic gradient) and the unsaturated conductivity at the particular soil moisture contents involved (25, 52, 71). Thus the field capacity condition will depend on the depth of wetting. Somewhat behind a wetting front after irrigation or rain ceases, the flow rate soon becomes slow because the change in tension with distance is small. This change plus the effect of gravity constitutes the driving force. With a great depth of wetting, the field capacity may be relatively high somewhat behind the front because the hydraulic gradient is small. On the other hand, if the amount of rainfall or irrigation is small, the depth wetted will be limited. The moisture soon spreads into the dry soil, and the wetting front "feathers out." Here the slow drainage condition of the field capacity is reached because the moisture conductivity is low at the moisture content in the limited depth zone behind the wetting front. In this case the observed field capacity will be at a relatively low moisture content.

The permanent wilting percentage will decrease with an increase in the salt content of the soil (2, 77, 78). Thus the range of available moisture decreases as the salt content of the soil increases. The range in total moisture stress for numerous soil-plant couples has been found usually to vary between 9 and 22 atmospheres (23), though a considerably wider range was found for 16 soils by Richards and his co-workers (63). In saline soils the salt concentration may increase until plants make little growth or fail to survive at moisture contents

near the field capacity. In the humid East, salinity is usually of little consequence. But salt damage due to heavy fertilization or irrigation with water from salty wells has been observed by the author, especially as the other component of moisture stress, the moisture tension, also has been allowed to increase.

Soil moisture flow rate will not only affect field capacity but has some effect on the lower soil moisture limit of extraction by plants. The permanent wilting percentage is not necessarily at a static equilibrium point between plant and soil forces; dynamic forces may also be involved. At moisture contents below the field capacity range, water movement is often very slow (25). Where absorptive roots are not concentrated in a mass of soil, there may be several atmospheres of pressure differential between plant leaves and soil moisture a few centimeters away from absorbing roots at average permanent wilting percentage. That is, one may often expect a moisture content and a moisture potential gradient to exist throughout a soil mass in which the roots of transpiring plants are growing. Breazeale and his co-workers (9) found that tomato plants would extract soil moisture somewhat below the normally observed permanent wilting percentage if air at 90 per cent relative humidity was passed through the soil. It should be noted that the air introduced was drier than the average condition of less mobile air in a soil at the permanent wilting percentage (usually considered to be above 98 per cent relative humidity). The circulating air probably furnished better moisture contact with the roots and eradicated the effect of potential gradients in the soil.

Moisture conductivity in sandy soils is high at low moisture tensions (15, 25, 54, 64) but very low at intermediate and high tensions. At high tensions in sandy soils the moisture films are mostly at the points of contact between soil grains, and moisture movement is principally in the vapor state. That is why sandy layers beneath finer textured soil act as moisture barriers. Water will move moderately fast in a medium textured soil at medium tensions, especially if the hydraulic gradient is large. Before water can spread rapidly as liquid into a sandy layer in the soil, it must accumulate in the adjacent soil until the tension is somewhat less than 0.5 atmosphere. Likewise, the conductivity of very loose soil at higher tensions is less than that of moderately compact soil. The popular notion that rapid water movement in soils is through worm holes, cracks, and channels does not hold for normal spreading of moisture in well-drained soils. This may be true for very wet soils with high water tables (15), but in well-drained soils, except for allowing the escape of entrapped air, numerous large channels may retard rather than facilitate the spreading of moisture.

Very fine textured soil, or very compact or frozen soil layers (17), will impede moisture movement and affect the available moisture supply in the soil. One may expect the tension gradient away from absorbing roots to be higher as plants approach wilting in very fine or very coarse textured soils than in soils of intermediate texture and structure. It is noteworthy that Richards (61) found the moisture sorption by a dry soil to be slower than the desorption (or drying) process for the same hydraulic gradient. This, in part, accounts for the high tension gradient at a wetting front.

Rooting depth and moisture storage are often limited by soil depth. Although the layer of rock beneath a shallow soil may be permeable enough to drain away excess water, rooting beyond the soil is limited to cracks and fissures in the rock. Likewise, rooting depth and available moisture supply may be limited when the water table fluctuates periodically between a level of a few feet below the surface and somewhat greater depths. Conditions in the Leon prairie soils of Florida vary seasonally between too wet and too dry for citrus, even though adequate frost protection may be provided by adjacent bodies of water.

The kinds of ions present in the soil solution and absorbed on the soil colloids may be toxic and so limit plant growth. Some may affect moisture movement and tension relationship by causing dispersion and swelling of the soil colloids.

Soil temperature is of consequence because it will affect both the growth vigor of the plant and the soil moisture tension relationships. Richards and Weaver (62) found that as the temperature is lowered, soils generally retain more water both at ⅓ atmosphere and at 15 atmospheres tension. But the difference or approximate available moisture quantity did not consistently increase or decrease with temperature for the soils studied. One would expect moisture conductivity to be increased with temperature and to affect moisture extraction to some degree. Temperature gradients will affect moisture supplies. As noted in the section on climatic factors, moisture will move in the vapor state from warm soil layers and condense in cooler zones (27).

Clearly, available moisture supply is not equally available to plants over the range from field capacity to permanent wilting percentage, though some few scientists persists in holding to this view (34, 76). From tension and conductivity considerations already discussed and from the volume of accumulated evidence (1, 2, 3, 5, 11, 16, 23, 28, 33, 39, 40, 41, 43, 45, 53, 56, 70, 72, 73, 74, 75, 77), it is clear that this view is untenable. As one should expect, moisture availability and plant growth decrease progressively as the wilting range is approached. Available moisture supply is not entirely a soil property. It is not a reservoir that holds just so much and no more. And not all of it is equally available to the plant until it is exhausted. Kelley (43) discussed reasons why some workers have been misled to believe in the equal availability theory. Foremost among the reasons he gave was that coarse textured soils hold most of their available water at tensions below 1 atmosphere. Even for medium textured soil the greater portion of the available moisture supply is exhausted at tensions below 4 atmospheres. Hence, plants growing on such soils will be under stresses above 1 to 4 atmospheres only about 10 to 20 per cent of the time. The effect of tension on availability can be studied better on finer textured soils that hold a fair portion of their available moisture near the wilting percentage.

Although growth response of plants generally decreases as the wilting point is approached, production of fruits, seeds, or other harvested parts may be increased by high rather than low moisture stress. According to Wadleigh and Richards (79), some plants make a physiological growth response to low moisture stress but fail to provide a corresponding economic return. Fruits of better eating or keeping qualities may often be produced at high moisture stress than at low

moisture stress. Rubber production by guayule is highest when the soil moisture stress approaches the permanent wilting range, though vegetative growth is greatest when the moisture stress is kept low by frequent irrigations.

Differences in availability of moisture to plants with change in tension have some interesting applications to crop production. Lehane and Staple (50, 70) have compared wheat production on sandy loams and clay loams of about equal available moisture supply. Wheat growing on coarse textured soil will grow rapidly and stool early in its life cycle to exhaust rapidly the moisture supply held at low tension, leaving little for the maturing processes of heading and filling. Wheat grown on finer textured soil will not grow so vigorously at first, but good moisture reserves will be left for the maturing processes. Seed production of some other crops is favored by moisture supplied during the maturing stage at relatively high tensions. The type and the quality of plants produced are influenced by soil moisture tension (11), and whether a low or high tension favors seed production will depend on the kind of plant (33).

Factors that affect available moisture storage capacity

Several plant, climatic, and soil factors that affect the available moisture supply have been discussed. Among these were rooting habits, plant vigor, stages of growth, soil depth, and depth of wetting. Because of misleading statements regarding the benefits of organic matter and soil aggregation to available moisture storage capacity, this subject must be given some attention here. Some of the erroneous ideas regarding available moisture capacity arose from confusion of the early term "water-holding capacity" with "available water capacity." The early method for determining the former consisted in saturating a core and allowing it to drain, then measuring the moisture retained by the sample. Since the sample was no more than 2 or 3 inches high the value obtained came close to the total pore space and included the larger pores that are generally air-filled. Jamison (42) showed that, except for sandy soils, organic matter increases did not increase the capacity of a soil to store available water. Much of the water stored in organic materials is held in the tension range above wilting. Also, the amount held per unit volume is not so great as weight percentage values would indicate. Even the increase in available moisture storage in sandy

TABLE 1

Available moisture storage and air capacities of soils samples varying widely in texture

Soil Type	Available Moisture Capacity*	Air Capacity
	ml./100 ml.	*ml./100 ml.*
Lakeland sand	3	26
Hiwassee sandy loam	5	18
Commerce silt loam	16	24
Sharkey clay	14	6
Lloyd clay	15	15

* Based on moisture release between ⅓ and 15 atmosphere tensions.

soils is so small in relation to amount of organic matter increase as to be of no practical value—at least for its effect on this one property. Any small benefit may be more than offset by decreases in wettability.

Materials that bring about structural improvement increase air capacity but seem to have little or no beneficial effect on available moisture storage capacity, as shown by Jamison (42) and Peters, Hagan, and Bodman (59).

Soils of intermediate and fine texture have larger "available moisture storage capacities" than coarse textured soils (fig. 1 and table 1). Dispersed clays or clay loams usually release about as much "available moisture" between the ⅓ and 15 atmosphere tension points as do silt loams, but the latter can be expected to supply moisture to plant roots more readily because of better aeration and moisture conductivity at low moisture tensions. A silty clay loam may store a smaller quantity of available moisture, as based on the accepted tension limits of availability, than will a silt loam, since the voids that would store available water in a silt loam would be partly filled with clay particles in a silty clay loam. Aggregation and structure development in soils will increase the volume of large pores and improve aeration but will reduce the volume of pores that store moisture (42). Because of the improved environment, however, roots may extend into and more completely ramify a larger soil volume, with the result that effective soil improvement may increase the over-all available moisture supply for the crop. Puddling of clay soils will change the moisture tension characteristics (13, 58) and may appear to increase the available moisture storage as measured between ⅓ and 15 atmospheres tension (42). But because of poor aeration in a puddled soil, the roots of most crop plants fail to extend into and withdraw the water from the soil mass even though the moisture tension is low.

Soil compaction will affect available moisture storage capacity. At field capacity very loose soils have high air content but relatively low moisture storage.

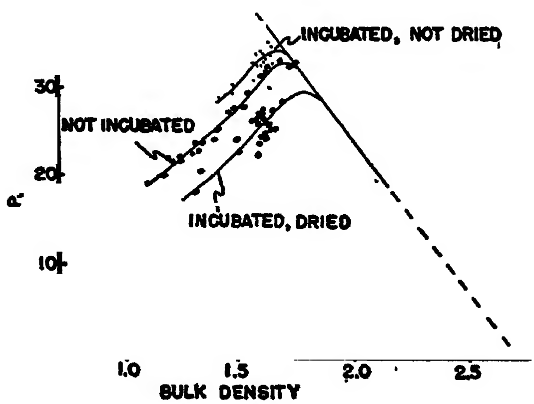

FIG. 2. VOLUME PERCENTAGE MOISTURE (P_v) AT ⅓ ATMOSPHERE MOISTURE TENSION FOR BRIQUETTES OF COMMERCE SILT LOAM BROUGHT TO VARYING BULK DENSITIES AND SUBJECTED TO VARIOUS TREATMENTS INCLUDING INCUBATION AND DRYING.

All samples were soaked 12 hours before subjection to ⅓ atmosphere for 24 hours on a ceramic pressure plate

Moderate compaction will increase available moisture storage capacity as well as unsaturated conductivity in the available moisture range for most soils. Soil disturbance may increase the moisture that a soil will hold between the ⅓ and 15 atmosphere points. The author found that soil briquettes allowed to incubate at low tension and room temperature for several weeks and then dried would hold less water at ⅓ atmosphere after being wetted than if undried or freshly compacted to the same bulk density. The effects of compaction, disturbance, and incubation and drying on the ⅓ atmosphere moisture are shown in figure 2. Plowing and tilling the soil may have other benefits than those usually given.

Soils react differently to wetting and to drying, different moisture contents being held at the same tensions for the two processes (64, pp. 73–251). This phenomenon has been referred to as hysteresis. Thus the degree of wetting, as well as the wetting depth, before drying proceeds may affect the moisture stored at field capacity.

Factors that affect moisture storage efficiency

Storage efficiency, or the proportion of moisture falling on the soil surface that will enter the surface and be stored in the soil, will depend not only on factors that affect available moisture storage capacity but also on plant interception, soil surface cover, soil surface structural stability, and presence of restricting layers near the surface. Hoover and his co-workers (38) found that in a loblolly pine forest only 86 per cent of the rainfall reached the soil surface and, of this, 20 per cent flowed down tree trunks. The present author believes that the dry soil bodies he observed under citrus trees in sandy soils of Florida were partly due to rainfall interception by the trees. On the other hand, grass sods or mulches generally increase efficiency through decreasing runoff. Kenworthy (44) found that after several years in sod the available moisture supply in the root zone averaged better than in plots that were clean-cultivated. He recommended the use of mulches because the grass would compete with the trees for soil moisture. Goodman (26), Pillsbury and Richards (60), Duley (18), and Fishbach and Duley (21) emphasized the importance of the soil surface to water intake. Fishbach and Duley found that, if a straw mulch protected the soil surface from sealing the claypans in several Nebraska soils did not appreciably retard downward movement of irrigation water. But the presence of very dense, compact or frozen layers near the surface (17) will cause water loss and erosion from melting snow or heavy rainfall. It should be emphasized here that even though treatments that increase air porosity and structural stability fail to benefit the available moisture storage capacity, if applied to the soil surface layers they may be expected to improve water intake and increase storage efficiency.

SUMMARY

Published information is cited to show that available soil moisture supply depends on plant and climatic factors as well as soil factors. Plant factors are drought resistance, rooting depth and ramification, plant vigor, and growth

stage. Climatic factors are evaporation and transpiration losses as influenced by air temperature, air humidity, fog, wind, and sunlight. Soil factors that affect available moisture supply are moisture tension relationships and osmotic pressure of the soil solutions (the two combined giving the total soil moisture stress); ions present in the soil solution and absorbed on the colloids; and soil moisture conductivity relationships, including the effect of wetting depth, soil temperature, and temperature gradients. The available moisture storage capacity is usually reduced by structural changes that decrease bulk density, including the effect of organic matter increases (except for sandy soils). Storage capacity of a soil that has remained in an undisturbed state for some time is usually increased by tillage if the soil is repacked to about the same bulk density. Soil briquettes incubated and dried and then rewetted failed to retain as much water at the ⅓ atmosphere tension as did similar samples undried or freshly compacted to the same bulk density. There may be other benefits from plowing and tilling the soil than those usually given. The importance of soil surface condition, including structural stability, in storage efficiency of rainfall and irrigation water is emphasized.

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CAPILLARY FRINGE AND FLOW OF WATER IN SOIL

DALE SWARTZENDRUBER AND DON KIRKHAM

Iowa Agricultural Experiment Station[1]

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According to Tolman (18), the capillary fringe is the "zone immediately above the water table in which water is held above the water table by capillarity." Childs (1) restricted the meaning of the term to that part of the zone which is essentially saturated with water, and it is in this restricted sense that the term "capillary fringe" is used in this paper. To designate the concept of Tolman's definition, the term "capillary region" is used herein.

Experiments with capillary siphons by Versluys (20) and McLaughlin (10) indicated that the capillary region could contribute substantially to the movement of water from a subsurface water table. Subsequent work by Wyckoff, Botset, and Muskat (21), Hooghoudt (5), and Donnan (3) indicated that the near-saturated part of the capillary region—the capillary fringe—was almost as efficient in conducting water, on a conductivity basis, as the region beneath the water table. In the three latter experiments, a satisfactory correction for fringe flow was obtained by considering the size of the conducting medium to have been increased by an addition of porous material equal in extent to the height of the fringe and equal in conductivity to that of the medium below the water table.

Vedernikov (19) analyzed theoretically a case of seepage from a canal into an ideal soil of infinite depth and found that under certain conditions the capillary fringe could increase seepage loss by as much as 120 per cent.

All these experiments indicated that a capillary fringe increased the flow, but Childs (1) in his work with electric analogues showed that in certain cases which involved the presence of a water table above tile drains the capillary fringe has a negligible effect upon the flow, although in another case (2), which involved the falling water table over tile drains, he found the recession of the top of the capillary fringe to be slower than the recession of the water table in the non-fringe case. This suggests that in some cases the presence of a capillary fringe not only fails to increase the flow but retards it.

Two different theoretical cases which elucidate observed capillary flow phenomena are discussed in this paper. In both, the flow is considered to occur in essentially water-saturated systems. In case 1 the flow is vertically downward; in case 2 it is primarily horizontal. The theory for case 2, although it is believed to be of value as it stands, was derived for a situation chosen as one which would lend itself well to experimental study; a later paper will report the experimental results for such a study.

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ANALYSIS FOR VERTICAL CASE

Horizontal falling water tables have been studied for sand by Lambe (7), and for some other soils by Luthin and Miller (8). The analysis here will be performed for a single vertical capillary tube with outlets into a constant-level water reservoir (fig. 1). Assume that water will rise in the tube to a height y_∞, but that initially the meniscus has been maintained at some height $y_0 > y_\infty$. In the process of complete drainage, the height of the meniscus drops from y_0 to y_∞. Let y represent the height of the meniscus at positions between y_0 and y_∞.

An expression for the flow rate q may be found from Poiseuille's law, $q = \pi r^4 \rho g(\Delta H)/8\eta L$, in which $\pi = 3.1416$, r = radius of capillary tube, ρ = density of water, g = acceleration of gravity, ΔH = hydraulic head difference, η = viscosity, and L = length of water column in the tube. By noting that the cross-sectional area $A = \pi r^2$, and defining the hydraulic conductivity $\bar{K} = r^2 \rho g/8\eta$, we find the law takes the form $q = \bar{K}A(\Delta H)/L$.

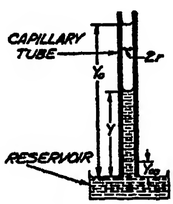

FIG. I

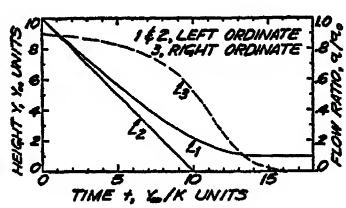

FIG. 2

FIG. 1. CAPILLARY TUBE MODEL OF FALLING WATER TABLE
FIG. 2. THEORETICAL CURVES BASED ON THE CAPILLARY TUBE MODEL

For the falling meniscus in the vertical tube, $q = \bar{K}A(y - y_\infty)/y$. If there is no capillary rise (that is, no fringe), $y_\infty = 0$, and $q_0 = \bar{K}A$, where q_0 is then the flow in the absence of a capillary fringe. Taking ratios between the q's results in:

$$q/q_0 = 1 - y_\infty/y \tag{1}$$

Equation (*1*) shows that only when $y \gg y_\infty$ does q/q_0 approach unity, the condition of no fringe effect. At finite values of y the ratio q/q_0 is less than unity, thus indicating a retardation in flow due to the capillary fringe.

By noting that the flow $q = -A\ dy/dt$, Poiseuille's law may be written as $dy/dt = -\bar{K}(1 - y_\infty/y)$. Separating variables, integrating, and supplying the initial conditions that $y = y_0$ when time $t = 0$, there results:

$$y_0 - y + y_\infty \ln \frac{y_0 - y_\infty}{y - y_\infty} = \bar{K}t \tag{2}$$

Equation (*2*) is shown graphically as curve 1 in figure 2, where y is plotted in units of y_∞ and y_0 is chosen as $10y_\infty$. Curve 2, a special case of equation (*2*), shows the linear relation which holds for the corresponding nonfringe case of $y_\infty = 0$. For early values of time the two curves are not greatly different, but as

time goes on they differ radically. In the fringe case represented by curve 1, the capillary tube never is completely drained. Furthermore, the height y approaches y_∞ asymptotically.

Curve 3 of figure 2 shows how the flow ratio q/q_0 varies with time. The plot was prepared from equations (*1*) and (*2*). Not only is q/q_0 always less than unity but it also decreases with time. Reference to equation (*1*) shows that, regardless of the initial value of y, q/q_0 cannot exceed unity.

Equation (*2*), except for a slight difference in variable, is equivalent to an expression derived by Horton (6) for a capillary tube inclined at an angle a to the horizontal. In Horton's expression, the term $\bar{K}t$ of equation (*2*) is multiplied by $\sin a$. In addition to the theoretical derivation, he also gave direct experimental confirmation for his equation, of which equation (*2*) is the special case for $a = 90°$.

Equations (*1*) and (*2*), because they are derived for a highly idealized case, cannot be applied indiscriminately to porous media. When equations (*1*) and (*2*) are compared against actual drainage of a vertical sand column[2] [data from Lambe (7)], the quantitative agreement is poor, but the retarding effect of the fringe is still shown clearly.

In the capillary tube, reduction in flow is caused by a reduced hydraulic gradient, which in turn is caused by the capillary fringe; that is, instead of a gradient $y/y = 1$, it is $(y - y_\infty)/y = 1 - y_\infty/y$. It is true, that for the same head difference the flow region is increased by the fringe, but this increase is brought about by increasing the length of the flow path; hence, the over-all hydraulic gradient is reduced.

If the size of the conducting medium is increased by extending it in a direction approximately perpendicular to the original lines of flow, the hydraulic head difference is not reduced across the original flow region. In this case, the presence of a capillary fringe increases the effective cross section for flow. It is this case which is the subject of the remainder of this paper.

ANALYSIS FOR HORIZONTAL CASE

The simplest case in which the capillary fringe adds flow region in a direction approximately perpendicular to the original flow lines in a porous medium is indicated in figure 3, in a manner which might be realized in a laboratory model. The porous medium, of adjustable height h, is contained between screens AA' and BB'. Water enters and leaves the porous medium across the boundaries AG and BC, respectively. No flow can occur across the boundaries of GF or $C'D$, since along these surfaces the pressure in the water is less than atmospheric. If such flow did take place, the outflow law as expressed by Richards (16) would be violated. Along the (small) surface CC' a surface of seepage will develop, but this seepage surface should be negligibly small if $\Delta H/L$ is kept equal to or less than 0.10. Since this surface of seepage is ignored in the analysis, all outflow is considered to occur across the outlet surface CB, and, accordingly, the phreatic surface, as shown in figure 3, will terminate very nearly at C.

[2] D. Swartzendruber. Capillary fringe and water flow in soil, p. 51, 1954. [Unpublished Ph.D. dissertation, Iowa State College, Ames.]

Initially, the height of medium h is equal to h_0, and the flow lines through the rectangular block $ABC'G$ (of unit thickness) are essentially horizontal. As h is made greater than h_0, additional conducting medium is added by the capillary fringe. With both ΔH and L unchanged, however, the over-all hydraulic gradient across the original block $ABC'G$ remains constant.

Recently Luthin and Day (9) studied a flow problem similar in some respects to that represented in figure 3. Their approach and method of analysis, however, are different from those given here.

Practically, figure 3 might be taken to represent the case of seepage through a rectangular earthen dam resting on a bedrock base, with $\Delta H/L$ kept small. Taking the upper boundary of the capillary fringe to be horizontal (as shown) is realistic, neglecting evaporation, because of the highly compacted and fine material used in dam construction. If the distance CD does not exceed the critical

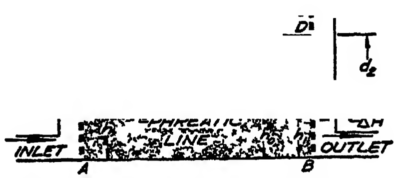

FIG. 3 SCHEMATIC SIDE VIEW OF HORIZONTAL FLOW MODEL

height required to maintain essential saturation, a draw-down curve at D, as might ordinarily be considered in a dam seepage problem, could be ignored, since dynamic draw-down forces would not sufficiently counteract the effect of the upward capillary pull.

Even if the upper boundary of the dam exceeds the critical capillary height, the upper boundary of the fringe will closely conform to the shape of the phreatic line. Since $\Delta H/L$ is small, the phreatic line, and hence the upper boundary of the fringe, will still be nearly horizontal. The applicability of the flow solution would in this case be limited to heights equal to or less than the critical capillary height.

Mathematical solution

General solution. In figure 3, assume that the hydraulic conductivity $\bar{K}$ is the same in the capillary fringe and in the region below the phreatic line (or water table). The solution is obtained by conformal mapping as outlined by Streeter (17) and applied by McNown and Hsu (11). The conformal transformation planes are shown in figure 4.

The Schwarz-Christoffel theorem is used to transform the interior of a polygon (that is, the flow region) in the z-plane into the upper half of the t-plane; and likewise for the polygon of complex potential in the w-plane. For the $z:t$ transformation the theorem is:

$$\frac{dz}{dt} = \frac{M}{(t - a_1)^{\alpha_1/\pi}(t - a_2)^{\alpha_2/\pi}} \tag{3}$$

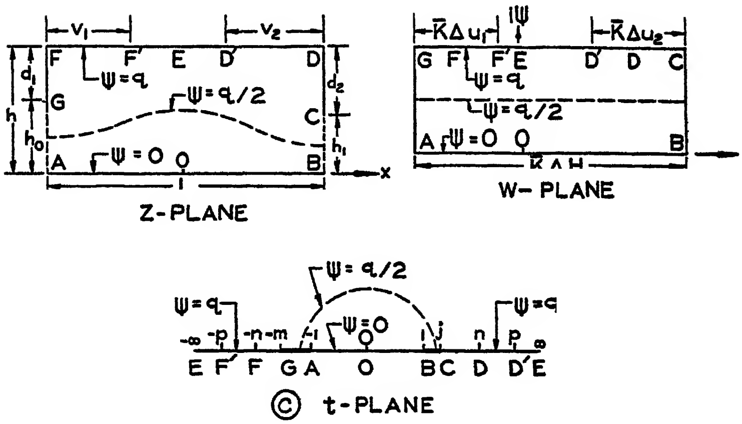

FIG. 4. CONFORMAL TRANSFORMATION PLANES

where M is a constant of proportionality, α_1 the exterior angle at one of the vertices of the polygon in the z-plane, and a_1 the corresponding point on the real axis of the t-plane. The theorem can be written similarly for the $w:t$ transformation with w replacing z. A different constant of proportionality must be used, however, and the α's must be correctly interpreted in the w-plane.

Applying equation (3) of figure 4a and c, and integrating from z_1 to z_2 and t_1 to t_2, we have:

$$z_2 - z_1 = M \int_{t_1}^{t_2} \frac{dt}{\sqrt{(t^2 - 1)(t^2 - n^2)}} \tag{4}$$

Similarly, for figure 4b and c we have:

$$w_2 - w_1 = N \int_{t_1}^{t_2} \frac{dt}{\sqrt{(t^2 - 1)(t + m)(t - j)}} \tag{5}$$

Equation (4) can be applied to line segments OB, BD, GF, and CD in figure 4a and c to obtain expressions for L, h, d_1, and d_2 respectively. The resulting integrals can be evaluated by formulas No. 536 and 540 in Peirce (15). Taking ratios to eliminate the M's, one finds that

$$\frac{L}{h} = \frac{2\,K[1/n]}{K[\sqrt{(n^2 - 1)/n^2}]}. \tag{6}$$

$$\frac{d_1}{h} \quad \frac{F[\sin^{-1}\sqrt{(n^2 - m^2)/(u^2 - 1)}, \sqrt{(n^2 - 1)/n^2}]}{K[\sqrt{(n^2 - 1)/n^2}]}. \tag{7}$$

$$\frac{d_2}{h} = \frac{F[\sin^{-1}\sqrt{(n^2 - j^2)/(n^2 - 1)}, \sqrt{(n^2 - 1)/n^2}]}{K[\sqrt{(n^2 - 1)/n^2}]} \tag{8}$$

in which K and F respectively are complete and incomplete elliptic integrals of the first kind. Both K and F have been tabulated by Legendre-Pearson (14). Dwight (4) has prepared a particularly useful tabulation of K.

Equation (5) is applied to line segments AB and AG in figure 4b and c to obtain expressions for $\bar{K}\Delta H$ and q respectively, where q is the total flow occurring for a height of medium h and is the maximum value of the stream function ψ. The resulting integrals are evaluated from Nos. 553 and 551 in Peirce (15). Next, on the basis of Darcy's law, define a reference flow $q_0 = \bar{K}(\Delta H)h_0/L$, where q_0 essentially reflects the flow in absence of a capillary fringe. Using these three equations, we have:

$$\frac{q}{q_0} = \frac{K[\sqrt{(m-1)(j-1)/(m+1)(j+1)}]}{K[\sqrt{2(m+j)/(m+1)(j+1)}]} \frac{L}{h_0} \tag{9}$$

The flow ratio q/q_0 is related to the geometrical ratios L/h, d_1/h, and d_2/h by the parametric equations (6), (7), (8), and (9). The parameters, which are real numbers, must satisfy the inequality $n > m > j > 1$. Hence, by using tabulated values, it is possible to calculate and plot q/q_0 as a function of h/h_0. Whether the added flow region retards, or has no effect upon, or increases the flow is indicated, respectively, by values of q/q_0 less than, or equal to, or greater than unity.

Anisotropy. Although the solution has been obtained by assuming the hydraulic conductivity $\bar{K}$ to be constant throughout the medium, the analysis is only slightly modified by introduction of a vertical hydraulic conductivity $\bar{K}_v$ different from the horizontal conductivity $\bar{K}_h$. In accordance with McNown and Hsu (11), a corrected length L' is calculated from the anisotropy relation:

$$L' = L\sqrt{\bar{K}_v/\bar{K}_h} \tag{10}$$

The value of L' is substituted in equation (6) in place of L; otherwise, the solution remains unchanged as long as the expression for flow is in the form q/q_0.

Infinite medium. As h/h_0 increases without bound, it seems reasonable that q/q_0 should approach a limiting value. This case can be investigated by placing at infinity the boundary $FF'ED'D$ in figure 4a. Then, instead of equation (4), the Schwarz-Christoffel theorem becomes:

$$z_2 - z_1 = M \int_{t_1}^{t_2} \frac{dt}{\sqrt{t^2 - 1}} \tag{11}$$

Applying equation (11) to the proper line segments in figure 4 in a similar manner as before yields:

$$m_1 = \cosh (h_0 \pi/L) \tag{12}$$

$$j_1 = \cosh (h_1 \pi/L) \tag{13}$$

where m_1 and j_1 are the limiting values of m and j, respectively. Since the complex potential diagram in figure 4b remains unchanged even if h/h_0 becomes infinite, the limiting value of q/q_0 can be calculated simply by substituting m_1 and j_1 in equation (9).

Distribution of head along upper boundary. It is of interest to calculate the distribution of hydraulic head along the boundary $FF'ED'D$ for finite values of h/h_0. For FE this may be done by applying, respectively, equations (4) and (5)

along the line segments FF' and GF' in figure 4. With No. 550 in Peirce (15) to evaluate the resulting integrals, and with the expressions for L and $\bar{K}\Delta H$ which were used in obtaining the general solution (equations (*6*) to (*9*)) one obtains, by taking ratios:

$$\frac{v_1}{L} = \frac{n}{n+1} \frac{F\left[\sin^{-1}\sqrt{\frac{(n+1)(p-n)}{2n(p-1)}}, \frac{2\sqrt{n}}{n+1}\right]}{K\,[1/n]} \tag{14}$$

$$\frac{\Delta u_1}{\Delta H} = \frac{F\left[\sin^{-1}\sqrt{\frac{(j+1)(p-m)}{(m+j)(p-1)}}, \sqrt{\frac{2(m+j)}{(m+1)(j+1)}}\right]}{K[\sqrt{2(m+j)/(m+1)(j+1)}]} \tag{15}$$

The quotient $\Delta u_1/\Delta H$ represents the fraction of the head ΔH which is used up at the point F'. The distance of F' from F is given in terms of the fraction v_1/L. Hence, for any given geometrical form specified by n, m, and j, it is possible to specify the fraction of head dissipated, $\Delta u_1/\Delta H$, for a point F' located anywhere along the boundary from F to E. The fraction of head undissipated (or the fraction of head remaining) is given by $1 - \Delta u_1/\Delta H$. To cover the range from F to E, the parameter p varies from n to infinity.

A similar analysis can be performed for the boundary DE with D' used in the same manner as F'. The result for $\Delta u_2/\Delta H$, which now is the fraction of head undissipated, is the same as equation (*15*) except that the positions of m and j are reversed. The expression for v_2/L is found to be identical to that for v_1/L.

Significance of the mathematical solution. The flow solution [equations (*6*) to (*9*)] enables one to determine whether the capillary fringe for a given porous material is as efficient in conducting water as is the region below the water table. For a model patterned after figure 3, one simply obtains an experimental curve of q/q_0 versus h/h_0 and compares it with the theoretical curve specified by equations (*6*) to (*9*).

Even without experimentation, the theoretical curves of q/q_0 versus h/h_0 are of value in that they specify the maximum contribution which the capillary fringe could make (when completely water-saturated) in a homogeneous soil.[3]

After the theory leading up to equations (*6*) to (*9*) was derived, it was found that by reducing certain results of Moulton (12) these four equations could be obtained for the flow of electricity in a rectangular conducting plate. After careful examination of Moulton's solution, it was decided, that for several reasons Moulton's results would not suffice for reference here. First his solution is more complex than is needed here, none of his examples cover the case of equations (*6*) to (*9*), and none of his formulas are in convenient form for the rather extensive numerical calculations needed for the problem at hand. Second, and basically

[3] In adjacent irrigation furrows, in which water stands at different levels, the lateral steady-state capillary seepage will be less than that indicated by the theory even if capillary saturation occurs, because the soil beneath the furrow bottoms will not be permeable. This statement will also be true for contour furrows as used in soil conservation practice unless the subsoil is more nearly impermeable than the soil between the furrows.

more important, Moulton's solution does not include the analysis for the distribution of the hydraulic head (in his case the electrical potential) along the boundaries of the flow medium. This head distribution is particularly useful in a study, as with tensiometers, of the actual head distribution along the upper boundary of a capillary fringe in an experimental model patterned after figure 3. Finally, Moulton's solution does not yield what corresponds in the present problem to the flow for an infinitely high capillary fringe and this result, since it gives the upper limit which a capillary fringe can contribute to flow, is important. Aside from these factors, Moulton's analysis is compressed, and references for missing steps are not given. From a consideration of these aspects of Moulton's analysis, it seemed clear to the authors that they must include here their own analysis.

Graphic illustration

Flow ratios of general solution. Curves of q/q_0 versus h/h_0, calculated from equations (*6*) to (*9*), are shown in figure 5. The imbalance of the flow net, $\Delta d = d_2 - d_1$, is equal to ΔH, the total head difference. The numerical values along the right-hand side of the diagram are limiting values of the flow ratio (q/q_0) curves calculated with the aid of equations (*12*) and (*13*). The straight line indicated by D represents the curve which would result if the flow contribution kept pace with the increase in volume of the flow region. The bending of curves A, B, B', C, and C' away from D illustrates the constricting effect of the geometry of flow. The value of the flow ratio, however, is always greater than unity whenever a capillary fringe is present, that is, for $h/h_0 > 1$. When $h_0 = L/10$, the fringe contribution reaches a maximum of 170 per cent of the flow beneath the water table.

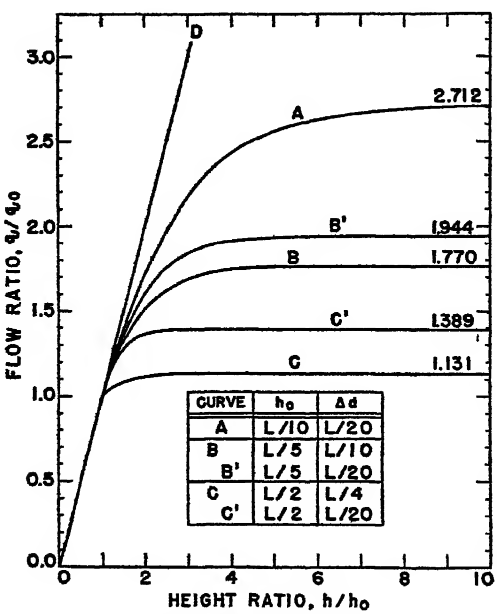

FIG. 5. THEORETICAL CURVES OF FLOW RATIO VERSUS HEIGHT RATIO

If the ratio of ΔH to the length L becomes too large, the system in figure 3 becomes similar to the dam case studied by Muskat (13), in which a surface of seepage forms on the vertical surface of the porous medium just above the outlet water level (in the vicinity of C, fig. 3). If an appreciable surface of seepage is formed, equations (*6*) to (*9*) and curves such as those in figure 5 will no longer apply. Perhaps at this point it should also be re-emphasized that the curves of figure 5 are based on the assumption of constant hydraulic conductivity throughout the medium.

The effect of anisotropy can be seen by introducing it into curve A of figure 5. Assume that the horizontal conductivity $\bar{K}_h$ is four times as great as the vertical conductivity $\bar{K}_v$. Applying equation (*10*), we find that $L' = L/2$. The box in figure 5 shows that, for curve A, $h_0 = L/10$ and $\Delta d = L/20$. With anisotropy, $h_0 = h'_0 = 2L'/10 = L'/5$, and $\Delta d = \Delta d' = 2L'/20 = L'/10$. When the primes are dropped, this is the case represented by curve B. Anisotropy of the kind here considered reduces the flow ratio. The reverse would be true if $\bar{K}_v$ were greater than $\bar{K}_h$.

It must be remembered that the curves of figure 5 are relative; that is, the value of q/q_0 depends not only on q but also q_0. In passing from curve A to curve C the reference flow q_0 increases by a factor of 5. Hence, it is instructive to investigate the behavior of the "pure fringe" contribution $q - q_0$ as a function of the height above the phreatic surface.

Fringe component of flow. For this purpose $\Delta d = \Delta H$ is considered to be very small so that d_2 is essentially equal to d_1, or also $h_1 \cong h_0$. From another viewpoint, one might visualize a case where $h_0 = h_1$, but in which a model as in figure 3 is raised slightly at A to obtain flow. The flow resulting from the presence of the capillary fringe is called q_c and is equal to $q - q_0$. The height above the phreatic surface is h_c, and is equal to $h - h_0$. The height h_c is plotted in terms of a constant unit of length, $L/100$, while q_c is plotted in terms of a constant flow q'_0, defined to be the saturated flow through a column of medium of height $L/100$. Figure 6 shows a series of these curves for various values of h_0. Again the calculations are ultimately based on equations (*6*) to (*9*).

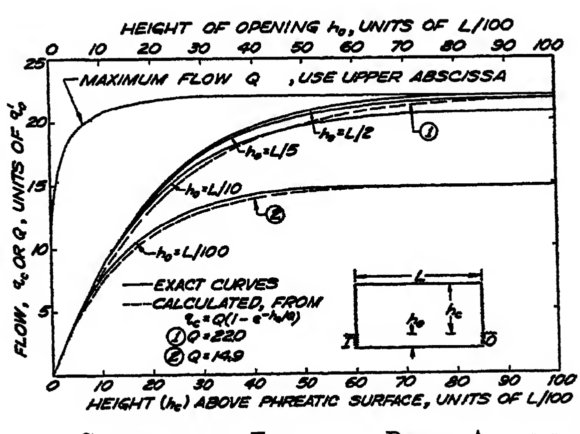

FIG. 6. THEORETICAL CURVES FOR THE FLOW IN THE REGION ABOVE THE WATER TABLE

Here it is seen that the fringe flow increases, in the absolute sense, as the size of the medium beneath the phreatic surface (specified by h_0) increases. The eventual leveling off within each curve, however, still reflects the constricting effect of the geometry of flow as h_c becomes large.

The curve for maximum fringe flow Q is simply the limiting value of $q - q_0$ (h_c infinite) plotted against h_0. When h_0 is 0, there is, of course, no flow, but as h_0 takes on finite values, the Q-curve rises very rapidly to a maximum and remains there.

The general form of the theoretical curves of q_c versus h_c (for various constant values of h_0) suggests that they might be approximated by the exponential relation $q_c = Q(1 - e^{-bh_c})$, in which b is a constant which must be appropriately fitted. This fitting is done by referring to figure 5 and noting that the slopes of the flow ratio curves are unity at $h/h_0 = 1$, or $h_c = 0$. Differentiating the exponential expression for q_c with respect to h_c, and setting $h_c = 0$ and $dq_c/dh_c = 1$, one finds that b equals the reciprocal of Q. Thus, the approximate relation is:

$$q_c = Q(1 - e^{-h_c/Q}) \tag{16}$$

Note that in the plotting scheme of figure 5, both h_c and Q are dimensionless quantities; hence, h_c/Q also is a dimensionless variable.

The broken-line curves 1 and 2 of figure 6, calculated from equation *(16)*, correspond respectively to the exact curves for $h_0 = L/2$ and $h_0 = L/100$. Obviously, the exponentials underestimate the true curves. For the $h_0 = L/2$ curve, the maximum error is about 8 per cent; for the $h_0 = L/100$ curve, it is about 4 per cent. It should be emphasized that equation *(16)* is merely an approximate and fitted relation; it is not the result of rigorous physical and mathematical considerations.

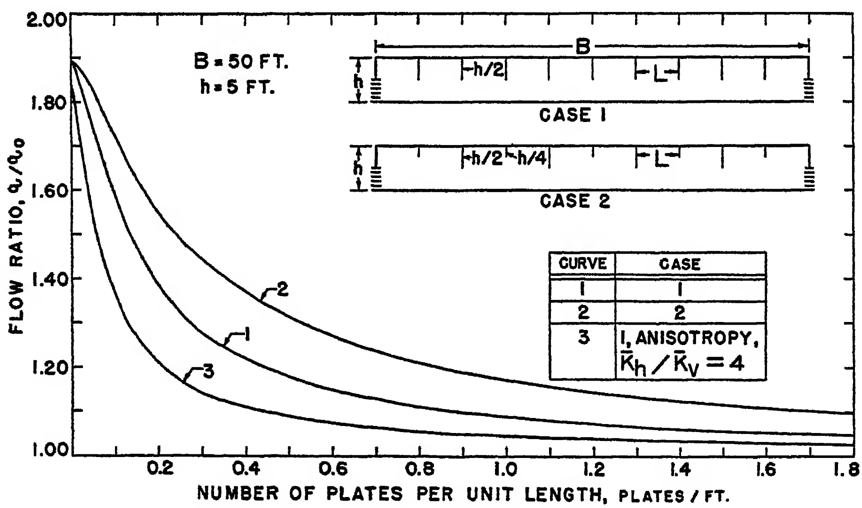

FIG. 7. FLOW AS AFFECTED BY BARRIERS IN THE FRINGE

Barriers in the fringe. The curves of figure 5 suggest that the capillary fringe can make an important contribution to total flow, particularly if the flow region is long with respect to its height. One may then ask what happens if barriers such as impermeable plates (approximating the effect of large pores or cracks in field soil) are inserted into the capillary fringe in the manner illustrated by cases 1 and 2 in figure 7. In both instances the height of the fringe is $h/2$. Again q_0 represents the flow without a capillary fringe, and q the total flow occurring when the fringe is present.

The solution for either case 1 or case 2 is simply the solution of a unit cell formed by the basic plate sequence. Case 2, for instance, is merely a repetition of the solution embodied in equations (*6*) to (*9*), in which $d_1/h = 1/4$, $d_2/h = 1/2$, and $L/h = B/h(n + 1)$, n being the number of plates in the distance B shown in the figure. Case 1 is even simpler, since $d_1 = d_2 = h_2$. The number of plates per unit length n/B is not strictly a continuous variable but is so indicated in figure 7 for simplicity.

Complete elimination of the fringe effect (that is, causing q/q_0 to equal unity) is difficult. The system represented by case 1 would require plates spaced 1 foot apart to reduce the fringe flow to about 9 per cent of the flow beneath the phreatic surface. The curve for the case 2 system shows that the interspersing of the short-length plates is relatively ineffective. On the other hand, curve 3 shows that the plate system is much more effective in an anisotropic soil ($\bar{K}_h > \bar{K}_v$) than in an isotropic one. If $\bar{K}_h$ were less than $\bar{K}_v$, the reverse would be true. Again, all of the results assume that the hydraulic conductivity is the same in the fringe as in the region below the phreatic surface.

SUMMARY

When a capillary fringe increases the length of each line of flow in a flow system without increasing the area perpendicular to the lines of flow, then the total flow through the system with the fringe will be less than it would be without the fringe. This behavior is qualitatively explainable on the basis of a vertical capillary tube model.

When a capillary fringe increases the size of a flow system in a direction perpendicular to the lines of flow as they exist without the fringe, then the total flow through the system with the fringe will be more than it would be without the fringe.

The latter case has been investigated theoretically for an isotropic system of constant hydraulic conductivity, in which the flow beneath the phreatic line (or water table) is essentially horizontal. An exact mathematical solution in elliptic integrals was obtained. Calculations show that when the region beneath the phreatic line is one tenth as high as it is long, the fringe contribution can reach a maximum of 170 per cent of the flow occurring beneath the phreatic line.

An exact mathematical solution for the horizontal flow model has also been obtained for anisotropic conditions. When the horizontal conductivity exceeds the vertical, the relative fringe contribution is reduced. If the vertical conductivity exceeds the horizontal, the reverse is true.

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Edafologia. Second Edition. By José M. Albareda Herrera and Angel Hoyos de Castro. Sociedad Anonima Española de Traductores y Autores, Madrid, 1955. Pp. 368, figs. 30. Price, 125 pesetas. Paper-bound.

The authors are members of the staffs of the Universities of Madrid and Granada, respectively. The book has three parts: formation and properties of soils, soil classification, and agricultural use of land. Factors of soil formation, the soil as a disperse system, clay minerals and their identification, physical and chemical properties of soils, organic matter relationships, and the liquid and gaseous phases of soils are covered in the first part. The second part deals with the great soil groups, with particular reference to the soils of Spain. The third part considers the soil as a natural source of nutrients, the use of fertilizers, manures, and liming materials, and methods of determining the chemical, physical, and biological status of soils in relation to crop needs. The material is well organized and presented. A number of interesting diagrams are shown, including one on soil development and another on phosphate fixation. A bibliography of some 50 books is appended. The book makes an important contribution to the literature on soils.

Farm Soils, Their Fertilization and Management. Fifth Edition. By Edmund L. Worthen and Samuel R. Aldrich. John Wiley and Sons, Inc., New York, 1956. Pp. 439, figs. 220, color plates 5. Price $4.95.

A substantial effort has gone into the revision of this book, which is now virtually a new publication. The illustrations tell much of the story better than it can be told by words. The purpose of the book is to give the reader, presumably a student in vocational agriculture or a farmer, the what, how, why, and when of the various practices employed in making land more productive. Some of its statements are debatable, if not incorrect, but one would not go far wrong if he followed the suggestions made by these two very capable and practical-minded men who have had a great deal of experience with soil and crop problems on the farms of New York State. The usefulness of the book is limited primarily to the 22 states included in the northeastern region for which it was designed. The authors have rendered real service in this further development of their publication.

The Presentation of Natural History Specimens. Volume 1. By Reginald Wagstaffe and J. Havelock Fidler. Philosophical Library, New York, 1955. Pp. 205, figs. 139. Price $10.

Techniques for the preservation of invertebrates, in both recent and fossil forms, have been brought together and published in this very convenient form. Specific instructions are given in working detail for 21 orders, with references for each order. Considerable space proportionately is given to the *Insecta*. The illustrations, drawn by Elizabeth M. Begg, are excellent. The appendix contains

supplemental information on apparatus, instruments, reagents, labeling, storage, and microscopy. A very useful book for those concerned with these problems.

Prosperity Beyond Tomorrow. By Samuel H. Ordway, Jr. The Ronald Press Company, New York, 1955. Pp. 208. Price $3.

The author, a lawyer and businessman now devoting most of his time to problems of natural resources, deals with leisure, pleasure, and plenty, which we are expected to enjoy to the end of the current century but are not so certain about beyond that point. The first two parts of the book on "The Impending Golden Age" and "The Field of Leisure" constitute a well-developed and highly interesting presentation of the at-hand and near-future well-being of the people of this nation. The author has hopes for the abandonment of war and for the creative use of our increasing leisure. The remainder of the book outlines the way to conservation, the need for it, and the basic issues involved. It considers our "technological destruction of the earth's resources" and a need for a change of emphasis toward preserving and increasing the productivity of our resource base. The author suggests that "dynamic devotion to sustained environmental prosperity may well provide a new and spiritual purpose in life." He concludes that in time we may have "to consume less raw material by reducing per capita consumption or by reducing the number of consumers or by doing both." For reducing the numbers "what is needed is a cheap, harmless, edible compound which will prevent conception for a period of one, two, or three weeks after it is eaten by either man or woman."

Studies in Use of Agricultural Limestone. By B. L. Elphick. Canterbury Agricultural College, Lincoln, New Zealand. Reprinted from *The New Zealand Journal of Science and Technology*, Volumes 36 and 37, 1954 and 1955. Pp. 65.

This is a series of three papers, constituting Research Publications 23, 35, and 37, which deal with the chemical and physical properties of limestones, solubility in acid soil as influenced by particle size, and solubility in acid soil as influenced by type of limestone and particle size. The papers extend the investigations of a number of workers in the United States. A solution equation was developed and tested on limestone products of various degrees of fineness and hardness. The author concludes that "particle size has been shown to be the preeminent factor, and for this reason differences in grinding needed by the hard and soft stones are less than the variation in limestone products would suggest."

The Editors

Photograph by Harvey B Kitchen

Herminie Broedel Kitchen Retires

With the publication of this issue, the highly capable assistance of Herminie Broedel Kitchen in editing SOIL SCIENCE is brought to a close. For 32 years she has served faithfully and efficiently, first as assistant editor and later as associate editor of the Journal. Her early editorial training was under the direction of Jacob G. Lipman, who founded SOIL SCIENCE in 1916 and served as its editor in chief until his death in 1939. In the interim between Dr. Lipman's death and the appointment of the present editor in chief in 1940, Mrs. Kitchen was given complete editorial responsibility for the Journal. Thus the best traditions of the Journal's past were carried forward to remain, as they are today, the guiding principles of its publication.

Throughout her long service Mrs. Kitchen has edited the many papers sympathetically yet competently. Her excellent training in the sciences, letters, and arts has been reflected in her work. Practically every paper submitted has been improved in some respect, but with careful preservation of the fundamental points of the author's presentation. Many of these papers required drastic revision to make them conform to the style and standards

set originally by SOIL SCIENCE and conscientiously adhered to over all the years of its publication. The English of many papers from foreign countries has virtually had to be translated into that of this country, which more frequently than not presented a very troublesome problem. Many of the papers published in SOIL SCIENCE, both from this country and abroad, were so capably handled in the required revisions that we have had a considerable number of highly complimentary letters from harassed writers, and even more harassed reviewers.

For many years Mrs. Kitchen and her husband have been torn between their desire to live out in the open country and their strong ties with the staff of the New Jersey Agricultural Experiment Station. Finally, a break with the past was made by the purchase of an old farmhouse up among the hills of Vermont, where they are now established and which they are now rapidly transforming into a very attractive and livable country home. As time and inclination permit, Mrs. Kitchen will devote her energies to developing agricultural science books for children and to writing and editorial work on a free-lance basis.

Some of those who have benefited from the careful editorial assistance of Mrs. Kitchen or who have known her in other capacities may be interested to know that her address is now South Royalton, Vermont. Any who may chance to pass that way will, we are sure, be cordially received at her home some two or three miles out from the village among the beautiful green—or snow-clad—hills.

We are indeed sorry to lose our day-to-day contact with such a cordial and capable person. But we were very fortunate in being able to obtain the services of Ruth Field, a well-trained editor, to take her place. Under the skillful direction of Mrs. Kitchen, she is now well prepared for this task. We are confident that Miss Field is capable of maintaining the high editorial standards that have been set for her.

FIRMAN E. BEAR

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